Chapter 5: Structures of Polymers

ISSUES TO ADDRESS...

• What are the general structural and chemical characteristics of polymer molecules?

• What are some of the common polymeric materials, and how do they differ chemically?

• How is the crystalline state in polymers different from that in metals and ceramics?
What is a Polymer?

Polymer

many repeat unit

Adapted from Fig. 5.2, Callister & Rethwisch 9e.

Polyethylene (PE)

Poly(vinyl chloride) (PVC)

Polypropylene (PP)

Adapted from Fig. 5.2, Callister & Rethwisch 9e.
Ancient Polymers

- Originally natural polymers were used
  - Wood
  - Cotton
  - Leather
  - Rubber
  - Wool
  - Silk

- Oldest known uses
  - Rubber balls used by Incas
  - Noah used pitch (a natural polymer) for the ark
Polymer Composition

Most polymers are hydrocarbons
  – i.e., made up of H and C
• Saturated hydrocarbons
  – Each carbon singly bonded to four other atoms
  – Example:
    • Ethane, C_2H_6
<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Structure</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>H—C—H</td>
<td>−164</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>H—C—C—H</td>
<td>−88.6</td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td>H—C—C—C—H</td>
<td>−42.1</td>
</tr>
<tr>
<td>Butane</td>
<td>C₄H₁₀</td>
<td>H—C—C—C—C—H</td>
<td>−0.5</td>
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<tr>
<td>Pentane</td>
<td>C₅H₁₂</td>
<td></td>
<td>36.1</td>
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<tr>
<td>Hexane</td>
<td>C₆H₁₄</td>
<td></td>
<td>69.0</td>
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</tbody>
</table>
Unsaturated Hydrocarbons

• Double & triple bonds somewhat unstable – can form new bonds
  – **Double bond** found in ethylene or ethene - $\text{C}_2\text{H}_4$
    
    ![Ethylene structure](image)

  – **Triple bond** found in acetylene or ethyne - $\text{C}_2\text{H}_2$
    
    ![Acetylene structure](image)
Isomerism

- Isomerism
  - two compounds with same chemical formula can have quite different structures

for example: \( \text{C}_8\text{H}_{18} \)
  - normal-octane

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H}
\end{align*}
\]

\[= \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \]

\[\downarrow \]

\[\text{H}_3\text{C}-\left(\text{CH}_2\right)_6\text{CH}_3 \]

- 2,4-dimethylhexane

\[
\begin{align*}
\text{CH}_3 \\
\text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_3
\end{align*}
\]

\[
\text{CH}_2 \\
\text{CH}_3
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Polymerization and Polymer Chemistry

- Free radical polymerization

\[ R^- + \text{monomer (ethylene)} \rightarrow R-C-C^- \] initiation

\[ R-C-C^- + \text{monomer (ethylene)} \rightarrow R-C-C-C-C^- \] propagation
dimer

- Initiator: example - benzoyl peroxide

\[ \text{benzoyl peroxide} \rightarrow 2 \text{phenyl} \] = 2 \( R^- \)
Chemistry and Structure of Polyethylene

Adapted from Fig. 5.1, Callister & Rethwisch 9e.

Note: polyethylene is a long-chain hydrocarbon - paraffin wax for candles is short polyethylene
### Bulk or Commodity Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Repeat Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (PE)</td>
<td>$\text{H} - \text{C} - \text{C} - \text{H}$</td>
</tr>
<tr>
<td>Poly(vinyl chloride) (PVC)</td>
<td>$\text{H} - \text{C} - \text{Cl}$</td>
</tr>
<tr>
<td>Polytetrafluoroethylene (PTFE)</td>
<td>$\text{F} - \text{C} - \text{C} - \text{F}$</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>$\text{H} - \text{C} - \text{C} - \text{H}$</td>
</tr>
<tr>
<td>Polystyrene (PS)</td>
<td>$\text{H} - \text{C} - \text{C} - \text{H}$</td>
</tr>
</tbody>
</table>
### Bulk or Commodity Polymers (cont)

**Table 5.3** (Continued)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Repeat Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(methyl methacrylate) (PMMA)</td>
<td>![PMMA structure]</td>
</tr>
<tr>
<td>Phenol-formaldehyde (Bakelite)</td>
<td>![Bakelite structure]</td>
</tr>
</tbody>
</table>
**Table 5.3 (Continued)**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Repeat Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(hexamethylene adipamide) (nylon 6,6)</td>
<td><img src="image" alt="diagram" /></td>
</tr>
<tr>
<td>Poly(ethylene terephthalate) (PET, a polyester)</td>
<td><img src="image" alt="diagram" /></td>
</tr>
<tr>
<td>Polycarbonate (PC)</td>
<td><img src="image" alt="diagram" /></td>
</tr>
</tbody>
</table>
MOLECULAR WEIGHT

- Molecular weight, $M$: Mass of a mole of chains.

Not all chains in a polymer are of the same length — i.e., there is a distribution of molecular weights.
MOLECULAR WEIGHT DISTRIBUTION

\[ \bar{M}_n = \frac{\text{total wt of polymer}}{\text{total # of molecules}} \]

\[ \bar{M}_n = \sum x_i M_i \]

\[ \bar{M}_w = \sum w_i M_i \]

\[ M_i = \text{mean (middle) molecular weight of size range } i \]

\[ x_i = \text{number fraction of chains in size range } i \]

\[ w_i = \text{weight fraction of chains in size range } i \]
**Molecular Weight Calculation**

Example: average mass of a class

<table>
<thead>
<tr>
<th># of Students</th>
<th>Weight mass (lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>104</td>
</tr>
<tr>
<td>1</td>
<td>116</td>
</tr>
<tr>
<td>2</td>
<td>140</td>
</tr>
<tr>
<td>1</td>
<td>143</td>
</tr>
<tr>
<td>4</td>
<td>180</td>
</tr>
<tr>
<td>5</td>
<td>182</td>
</tr>
<tr>
<td>2</td>
<td>191</td>
</tr>
<tr>
<td>2</td>
<td>220</td>
</tr>
<tr>
<td>1</td>
<td>225</td>
</tr>
<tr>
<td>1</td>
<td>380</td>
</tr>
</tbody>
</table>

What is the average weight of the students in this class:

a) Based on the number fraction of students in each mass range?

b) Based on the weight fraction of students in each mass range?
Molecular Weight Calculation (cont.)

Calculate the number fractions and weight fractions of students in each weight as follows:

\[
x_i = \frac{N_i}{\sum N_i} \quad \text{and} \quad w_i = \frac{N_i W_i}{\sum N_i W_i}
\]

- Total number = 20
- Total weight = 3,700 lb

For example: for the 180 lb students

\[
x_{180} = \frac{4}{20} = 0.2
\]

\[
w_{180} = \frac{4 \times 180}{3700} = 0.195
\]
### Molecular Weight Calculation (cont.)

<table>
<thead>
<tr>
<th># of Students</th>
<th>Weight mass (lb)</th>
<th>Number Fractions ($x_i$)</th>
<th>Weight Fractions ($w_i$)</th>
<th>$x_iM_i$</th>
<th>$w_iM_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>104</td>
<td>1/20=0.05</td>
<td>(104x1)/3,700=0.028</td>
<td>0.05x104=5.2</td>
<td>0.028x104=2.912</td>
</tr>
<tr>
<td>1</td>
<td>116</td>
<td>1/20=0.05</td>
<td>(116x1)/3,700=0.031</td>
<td>0.05x116=5.8</td>
<td>0.031x116=3.596</td>
</tr>
<tr>
<td>2</td>
<td>140</td>
<td>2/20=0.10</td>
<td>(140x2)/3,700=0.076</td>
<td>0.10x140=14.0</td>
<td>0.076x140=10.64</td>
</tr>
<tr>
<td>1</td>
<td>143</td>
<td>1/20=0.05</td>
<td>(143x1)/3,700=0.039</td>
<td>0.05x143=7.15</td>
<td>0.039x143=5.577</td>
</tr>
<tr>
<td>4</td>
<td>180</td>
<td>4/20=0.20</td>
<td>(180x4)/3,700=0.195</td>
<td>0.20x180=36.0</td>
<td>0.195x180=35.10</td>
</tr>
<tr>
<td>5</td>
<td>182</td>
<td>5/20=0.25</td>
<td>(182x5)/3,700=0.246</td>
<td>0.25x182=45.5</td>
<td>0.246x182=44.772</td>
</tr>
<tr>
<td>2</td>
<td>191</td>
<td>2/20=0.10</td>
<td>(191x2)/3,700=0.103</td>
<td>0.10x191=19.1</td>
<td>0.103x191=19.673</td>
</tr>
<tr>
<td>2</td>
<td>220</td>
<td>2/20=0.10</td>
<td>(220x2)/3,700=0.119</td>
<td>0.10x220=22.0</td>
<td>0.119x220=26.18</td>
</tr>
<tr>
<td>1</td>
<td>225</td>
<td>1/20=0.05</td>
<td>(225x1)/3,700=0.061</td>
<td>0.05x225=11.25</td>
<td>0.061x225=13.725</td>
</tr>
<tr>
<td>1</td>
<td>380</td>
<td>1/20=0.05</td>
<td>(380x1)/3,700=0.103</td>
<td>0.05x380=19.0</td>
<td>0.103x380=39.14</td>
</tr>
</tbody>
</table>

**Total # 20**

**Total weight 3,700 lb**

\[
\overline{M}_n = \sum x_iM_i = 185 \text{ lb}
\]

\[
\overline{M}_w = \sum w_iM_i = 201 \text{ lb}
\]
Degree of Polymerization, \( DP \)

\[ DP = \text{average number of repeat units per chain} \]

\[ H - C - C - (C - C) - C - C - C - C - C - C - C - H \]

\[ DP = 6 \]

\[ DP = \frac{\bar{M}_n}{\bar{m}} \]

where \( \bar{m} = \text{average molecular weight of repeat unit} \)

for copolymers this is calculated as follows:

\[ \bar{m} = \sum f_i m_i \]

Chain fraction \( f_i \) mol. wt of repeat unit \( i \)
Molecular Structures for Polymers

- Linear
- Branched
- Cross-Linked
- Network

Adapted from Fig. 5.7, Callister & Rethwisch 9e.
Polymers – Molecular Shape

**Conformation** – chain bending and twisting are possible by rotation of carbon atoms around their chain bonds, conformation encompasses portions of a molecule which are not directly linked to the same atom

note: not necessary to break chain bonds to alter molecular shape

*Thermal energy at room temperature is sufficient to rotate some simple covalent bonds.*

Adapted from Fig. 5.5, *Callister & Rethwisch 9e.*
Molecular Configurations for Polymers

Configurations – arrangements of units along the axis of the chain. Atom positions are not alterable except by breaking and re-forming primary bonds. *This costs a lot of energy!!*

*R: atom or side group other than H (Cl, CH₃ etc.)*
**Isomerism**
Different atomic configurations are possible for polymers with the same composition

**Stereoisomerism:** Atoms are linked together in the spatial arrangement in the same order but differ in their spatial arrangement.
- R groups* are situated on the same side of the chain (**isotactic** configuration)
- R groups alternate sides of the chain (**syndiotactic** configuration)
- R groups randomly position (**atactic** configuration)

**Geometrical Isomerism:** Repeat units have a carbon double bond. A side group is bonded to each of the carbon atoms participating in the double bond, which may be situated on one side of the chain (**cis**) or its opposite (**trans**).
Stereoisomerism

**Tacticity** — stereoregularity or spatial arrangement of \( R \) units along chain

- **isotactic** — all \( R \) groups on same side of chain
- **syndiotactic** — \( R \) groups alternate sides

**Diagram:**

- Isotactic: All \( R \) groups are on the same side of the chain.
- Syndiotactic: \( R \) groups alternate on opposite sides of the chain.
Tacticity (cont.)

atactic – R groups randomly positioned

\[ \begin{array}{cccccccccc}
H & H & H & H & H & H & R & H & H & H \\
\hline
H & R & H & R & H & H & H & H & R \\
\end{array} \]
Geometrical (cis/trans) Isomerism

**cis**
- **cis-isoprene** (natural rubber)
- H atom and CH₃ group on same side of chain

**trans**
- **trans-isoprene** (gutta percha)
- H atom and CH₃ group on opposite sides of chain

![cis-trans isomerism](image-url)
Copolymers

two or more monomers polymerized together

- **random** – A and B randomly positioned along chain
- **alternating** – A and B alternate in polymer chain
- **block** – large blocks of A units alternate with large blocks of B units
- **graft** – chains of B units grafted onto A backbone
Polymer Crystals

- Crystalline regions
  - thin platelets with chain folds at faces
  - Chain folded structure

Fig. 5.11, Callister & Rethwisch 9e.
Polymer Crystals (cont.)

Polymers rarely 100% crystalline

- Difficult for all regions of all chains to become aligned

- Degree of crystallinity expressed as % crystallinity.
  -- Some physical properties depend on % crystallinity.
  -- Heat treating causes crystalline regions to grow and % crystallinity to increase.

Fig. 14.11, Callister 6e. (From H.W. Hayden, W.G. Moffatt, and J. Wulff, The Structure and Properties of Materials, Vol. III, Mechanical Behavior, John Wiley and Sons, Inc., 1965.)
Polymer Single Crystals

- Electron micrograph – multilayered single crystals (chain-folded layers) of polyethylene
- **Single crystals** – only for slow and carefully controlled growth rates

Fig. 5.10, Callister & Rethwisch 9e.
Semicrystalline Polymers

- Some semicrystalline polymers form spherulite structures
- Alternating chain-folded crystallites and amorphous regions
- Spherulite structure for relatively rapid growth rates

Fig. 5.12, Callister & Rethwisch 9e.