CHAPTER 4: POLYMER STRUCTURES

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. 4.2, Callister & Rethwisch 3e.

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$_2$H$_6$

![Ethane Structure](image)

Table 4.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: C$_n$H$_{2n+2}$

<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>CH$_4$</td>
<td>H—C—H</td>
<td>-164</td>
</tr>
<tr>
<td>Ethane</td>
<td>C$_2$H$_6$</td>
<td>H—C—H</td>
<td>-88.6</td>
</tr>
<tr>
<td>Propane</td>
<td>C$_3$H$_8$</td>
<td>H—C—C—H</td>
<td>-42.1</td>
</tr>
<tr>
<td>Butane</td>
<td>C$<em>4$H$</em>{10}$</td>
<td>H—C—C—H—C—H</td>
<td>-0.5</td>
</tr>
<tr>
<td>Pentane</td>
<td>C$<em>5$H$</em>{12}$</td>
<td>H—C—C—C—H</td>
<td>36.1</td>
</tr>
<tr>
<td>Hexane</td>
<td>C$<em>6$H$</em>{14}$</td>
<td>H—C—C—C—C—H</td>
<td>69.0</td>
</tr>
</tbody>
</table>
**Unsaturated Hydrocarbons**

- Double & triple bonds somewhat unstable
  - can form new bonds
    - **Double bond** found in ethylene or ethene - $C_2H_4$
      $$\text{H} \hspace{1cm} \text{C}=\text{C} \hspace{1cm} \text{H}$$

    - **Triple bond** found in acetylene or ethyne - $C_2H_2$
      $$\text{H} \hspace{0.25cm} \text{C}≡\text{C} \hspace{0.25cm} \text{H}$$

**Isomerism**

- **Isomerism**
  - two compounds with same chemical formula can have quite different structures
    - for example: $C_8H_{18}$
      - normal-octane
        $$\text{H} \hspace{0.25cm} \text{H} \hspace{0.25cm} \text{H} \hspace{0.25cm} \text{H} \hspace{0.25cm} \text{H} \hspace{0.25cm} \text{H} \hspace{0.25cm} \text{H} \hspace{0.25cm} \text{H}$$
      $$\Rightarrow H_3C\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$$

      - 2,4-dimethylhexane
        $$\text{CH}_3$$
        $$\text{H}_2\text{C}≡\text{CH}\text{-CH}_2\text{-CH}_2\text{-CH}_3$$
        $$\text{CH}_3$$
        $$\text{CH}_3$$
Polymerization and Polymer Chemistry

- **Free radical polymerization**
  
  $R^\cdot + \text{monomer (ethylene)} \rightarrow R\text{-dimmer}$

- **Initiator**: example - benzoyl peroxide

Chemistry and Structure of Polyethylene

- Adapted from Fig. 4.1, Callister & Rethwisch 3e.

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

## Table 4.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Repeat Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (PE)</td>
<td>( \text{H} - \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{F} )</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>( \text{H} - \text{C} - \text{CH}_3 )</td>
</tr>
</tbody>
</table>

## Bulk or Commodity Polymers (cont)

## Table 4.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Repeat Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene (PS)</td>
<td>( \text{H} - \text{C} - \text{C} - )</td>
</tr>
<tr>
<td>Poly(methyl methacrylate) (PMMA)</td>
<td>( \text{H} - \text{C} - \text{O} - \text{CH}_3 )</td>
</tr>
<tr>
<td>Phenol-formaldehyde (Bakelite)</td>
<td>( \text{C}_6\text{H}_4\text{OH} - \text{CH}_2\text{CH}_3 )</td>
</tr>
</tbody>
</table>
Bulk or Commodity Polymers (cont)

### Table 4.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Repeat Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(hexamethylene adipamide) (nylon 6,6)</td>
<td>![Image]</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate) (PET, a polyester)</td>
<td>![Image]</td>
</tr>
<tr>
<td>Polycarbonate (PC)</td>
<td>![Image]</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

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

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

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

- \(M_i\) = mean (middle) molecular weight of size range \(i\)
- \(x_i\) = number fraction of chains in size range \(i\)
- \(w_i\) = weight fraction of chains in size range \(i\)

**Adapted from Fig. 4.4, Callister & Rethwisch 3e.**

### Molecular Weight Calculation

**Example: average mass of a class**

<table>
<thead>
<tr>
<th>Student</th>
<th>Weight mass (lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>104</td>
</tr>
<tr>
<td>2</td>
<td>116</td>
</tr>
<tr>
<td>3</td>
<td>140</td>
</tr>
<tr>
<td>4</td>
<td>143</td>
</tr>
<tr>
<td>5</td>
<td>180</td>
</tr>
<tr>
<td>6</td>
<td>182</td>
</tr>
<tr>
<td>7</td>
<td>191</td>
</tr>
<tr>
<td>8</td>
<td>220</td>
</tr>
<tr>
<td>9</td>
<td>225</td>
</tr>
<tr>
<td>10</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?
**Solution:** The first step is to sort the students into weight ranges. Using 40 lb ranges gives the following table:

<table>
<thead>
<tr>
<th>weight range</th>
<th>number of students</th>
<th>mean weight</th>
<th>Calculate the number and weight fraction of students in each weight range as follows:</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass (lb)</td>
<td>( N_i )</td>
<td>( W_i )</td>
<td>( x_i = \frac{N_i}{\sum N_i} ) ( w_i = \frac{N_i W_i}{\sum N_i W_i} )</td>
</tr>
<tr>
<td>81-120</td>
<td>2</td>
<td>110</td>
<td>( x_{81-120} = \frac{2}{10} = 0.2 ) ( w_{81-120} = \frac{2 \times 110}{1881} = 0.117 )</td>
</tr>
<tr>
<td>121-160</td>
<td>2</td>
<td>142</td>
<td></td>
</tr>
<tr>
<td>161-200</td>
<td>3</td>
<td>184</td>
<td></td>
</tr>
<tr>
<td>201-240</td>
<td>2</td>
<td>223</td>
<td></td>
</tr>
<tr>
<td>241-280</td>
<td>0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>281-320</td>
<td>0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>321-360</td>
<td>0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>361-400</td>
<td>1</td>
<td>380</td>
<td></td>
</tr>
</tbody>
</table>

\[\sum N_i = 10\] \[\sum N_i W_i = 1881\] total number total weight

\[
\overline{M_n} = \sum x_i M_i = (0.2 \times 110 + 0.2 \times 142 + 0.3 \times 184 + 0.2 \times 223 + 0.1 \times 380) = 188 \text{ lb}
\]

\[
\overline{M_w} = \sum w_i M_i = (0.117 \times 110 + 0.150 \times 142 + 0.294 \times 184 + 0.237 \times 223 + 0.000 \times 380) = 218 \text{ lb}
\]
Degree of Polymerization, $DP$

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

$DP = 6$

$DP = \frac{M_n}{m}$

where $m = \text{average molecular weight of repeat unit}$

for copolymers this is calculated as follows:

$\overline{m} = \sum f_i m_i$

$\text{Chain fraction}$

$\text{mol. wt of repeat unit } i$

Molecular Structures for Polymers

Adapted from Fig. 4.7, Callister & Rethwisch 3e.
Polymers – Molecular Shape

Molecular Shape (or Conformation) – chain bending and twisting are possible by rotation of carbon atoms around their chain bonds

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

Adapted from Fig. 4.5, Callister & Rethwisch 3e.

Chain End-to-End Distance, $r$

Adapted from Fig. 4.6, Callister & Rethwisch 3e.
Molecular Configurations for Polymers

Configurations – to change must break bonds

- Stereoisomerism

Stereoisomers are mirror images – can’t superimpose without breaking a bond

Tactility

Tactility – stereoregularity or spatial arrangement of \( R \) units along chain

- Isotactic – all \( R \) groups on same side of chain
- Syndiotactic – \( R \) groups alternate sides
**Tacticity (cont.)**

atactic – R groups randomly positioned

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

**cis/trans Isomerism**

cis

- cis-isoprene (natural rubber)
- H atom and \(\text{CH}_3\) group on same side of chain

trans

- trans-isoprene (gutta percha)
- H atom and \(\text{CH}_3\) group on opposite sides of chain
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

\[
A - . \quad B - .
\]

Adapted from Fig. 4.9, Callister & Rethwisch 3e.

Crystallinity in Polymers

- Ordered atomic arrangements involving molecular chains
- Crystal structures in terms of unit cells
- Example shown – polyethylene unit cell

Adapted from Fig. 4.10, Callister & Rethwisch 3e.
Polymer Crystallinity

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

![Diagram of polymer crystallinity](image)

Adapted from Fig. 4.12, Callister & Rethwisch 3e.

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.

![Diagram of polymer crystallinity](image)

Adapted from Fig. 4.11, Callister 6e. (Fig. 14.11 is 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

Adapted from Fig. 4.11, Callister & Rethwisch 3e.

Semicrystalline Polymers

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

Adapted from Fig. 4.13, Callister & Rethwisch 3e.
Photomicrograph – Spherulites in Polyethylene

Cross-polarized light used
-- a maltese cross appears in each spherulite

Adapted from Fig. 4.14, Callister & Rethwisch 3e

Materials Science - Prof. Choi, Hae-Jin  Chapter 4 – 33