CHAPTER 14: POLYMER STRUCTURES

ISSUES TO ADDRESS...

• What are the basic microstructural features?

• How are polymer properties effected by molecular weight?

• How do polymeric crystals accommodate the polymer chain?
Chapter 14 – Polymers

What is a polymer?

Polymer = many repeat units

Polyethylene (PE)

Polyvinyl chloride (PVC)

Polypropylene (PP)

Adapted from Fig. 14.2, Callister 7e.

Macromolecules
Polymer Composition

Hydrocarbon

Most polymers are hydrocarbons
  – i.e. made up of H and C
• Saturated hydrocarbons
  – Each carbon bonded to four other atoms

\[
\text{C}_n\text{H}_{2n+2}
\]
<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>CH₄</td>
<td>H─C─H</td>
<td>-164</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>H─C─C─H</td>
<td>-88.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td>H─C─C─C─H</td>
<td>42.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butane</td>
<td>C₄H₁₀</td>
<td></td>
<td>-0.5</td>
</tr>
<tr>
<td>Pentane</td>
<td>C₅H₁₂</td>
<td></td>
<td>36.1</td>
</tr>
<tr>
<td>Hexane</td>
<td>C₆H₁₄</td>
<td></td>
<td>69.0</td>
</tr>
</tbody>
</table>
Unsaturated Hydrocarbons

- Double & triple bonds relatively reactive – can form new bonds
  - *Double bond* – ethylene or ethene - $C_nH_{2n}$
    
    \[
    \begin{array}{c}
    \text{H} \\
    \text{C=\text{C}} \\
    \text{H} \\
    \text{H}
    \end{array}
    \]
  
  - *Triple bond* – acetylene or ethyne - $C_nH_{2n-2}$
    
    \[
    \begin{array}{c}
    \text{H} \\
    \text{C≡\text{C}} \\
    \text{H}
    \end{array}
    \]

- 4-bonds, but only 3 atoms bound to C’s
Isomerism

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

**Ex: C₄H₁₀**
- Butane
  
  \[ T_{\text{boiling}} = -0.5^\circ C \]

- Isobutane
  
  \[ T_{\text{boiling}} = -12.3^\circ C \]
Isomerism

Ex: C₈H₁₈

- n-octane

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

\[\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_3 \\
\downarrow & \quad & \quad & \quad & \quad & \quad & \quad & \quad \\
\text{H}_3\text{C} & \quad (\text{CH}_2)_6 & \text{CH}_3
\end{align*}\]

- 2-methyl-4-ethyl pentane (isooctane)

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 & \quad \text{CH} & \quad \text{CH} & \quad \text{CH}_3 \\
\quad & \quad & \quad & \quad & \quad \\
\quad & \quad & \quad & \quad & \quad \\
\quad & \quad & \quad & \quad & \quad \\
\quad & \quad & \quad & \quad & \quad \\
\text{CH}_3 & \quad \text{CH}_2 & \quad \text{C} & \quad \text{CH}_3
\end{align*}
\]

- 2,2,4-trimethylpentane (isooctane)
Polymer molecules and Chemistry

• Free radical polymerization

\[ \text{R} \cdot + \text{C} = \text{C} \quad \rightarrow \quad \text{R} - \text{C} = \text{C} \cdot \]

initiation

Unpaired electron

Chapter 14 - 8

• Initiator: \( \text{R} \cdot \ \text{CH}_3, \ \text{C}_2\text{H}_5, \ \text{C}_6\text{H}_5 \) (methyl, ethyl, phenyl)

example - benzoyl peroxide

\[ \text{H} - \text{C} = \text{O} - \text{O} - \text{C} - \text{H} \quad \rightarrow \quad 2 \quad \text{H} - \text{C} = \text{O} \cdot \quad = 2 \text{R} \cdot \]
Chemistry of Polymers

Adapted from Fig. 14.1, Callister 7e.

Repeat unit

ethylene \rightarrow \text{polyethylene}

or

\text{polyethylene}
Chemistry of Polymers

tetrafluoroethylene \( \rightarrow \) polytetrafluoroethylene (PTFE)

vinyl chloride \( \rightarrow \) poly vinyl chloride (PVC)
# Bulk or Commodity Polymers

## Table 14.3: 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>[Image]</td>
</tr>
<tr>
<td>Poly(vinyl chloride) (PVC)</td>
<td>[Image]</td>
</tr>
<tr>
<td>Polytetrafluoroethylene (PTFE)</td>
<td>[Image]</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>[Image]</td>
</tr>
<tr>
<td>Polymer</td>
<td>Repeat Unit</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>Polystyrene (PS)</td>
<td><img src="image" alt="Polystyrene Repeat Unit" /></td>
</tr>
<tr>
<td>Poly(methyl methacrylate) (PMMA)</td>
<td><img src="image" alt="PMMA Repeat Unit" /></td>
</tr>
<tr>
<td>Phenol-formaldehyde (Bakelite)</td>
<td><img src="image" alt="Bakelite Repeat Unit" /></td>
</tr>
<tr>
<td>Polymer</td>
<td>Repeat Unit</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>Poly(hexamethylene adipamide) (nylon 6,6)</td>
<td><img src="image1" alt="Polymer Structure" /></td>
</tr>
<tr>
<td>Poly(ethylene terephthalate) (PET, a polyester)</td>
<td><img src="image2" alt="Polymer Structure" /></td>
</tr>
<tr>
<td>Polycarbonate (PC)</td>
<td><img src="image3" alt="Polymer Structure" /></td>
</tr>
</tbody>
</table>
MOLECULAR WEIGHT

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

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

Adapted from Fig. 14.4, Callister 7e.

$\bar{M}_n$ is more sensitive to higher molecular weights

Weight-average, $\bar{M}_w$ is more sensitive to higher molecular weights

Adapted from Fig. 14.4, Callister 7e.
Molecular Weight Calculation

Example: average mass of a class

<table>
<thead>
<tr>
<th>( N_i )</th>
<th>( M_i )</th>
<th>( x_i )</th>
<th>( w_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td># of students</td>
<td>mass (lb)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>0.1</td>
<td>0.054</td>
</tr>
<tr>
<td>1</td>
<td>120</td>
<td>0.1</td>
<td>0.065</td>
</tr>
<tr>
<td>2</td>
<td>140</td>
<td>0.2</td>
<td>0.151</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>0.3</td>
<td>0.290</td>
</tr>
<tr>
<td>2</td>
<td>220</td>
<td>0.2</td>
<td>0.237</td>
</tr>
<tr>
<td>1</td>
<td>380</td>
<td>0.1</td>
<td>0.204</td>
</tr>
</tbody>
</table>

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

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

\[
\begin{array}{cc}
\bar{M}_n & \bar{M}_w \\
186 lb & 216 lb
\end{array}
\]
Degree of Polymerization, $DP$

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

$DP = 6$

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

where $m = \text{molecular weight of repeat unit}$
Degree of Polymerization, $DP$

Average molecular weights and DP [poly(vinyl chloride)]

<table>
<thead>
<tr>
<th>Molecular Weight Range (g/mol)</th>
<th>Mean $M_i$ (g/mol)</th>
<th>$x_i$</th>
<th>$x_iM_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,000–10,000</td>
<td>7,500</td>
<td>0.05</td>
<td>375</td>
</tr>
<tr>
<td>10,000–15,000</td>
<td>12,500</td>
<td>0.16</td>
<td>2000</td>
</tr>
<tr>
<td>15,000–20,000</td>
<td>17,500</td>
<td>0.22</td>
<td>3850</td>
</tr>
<tr>
<td>20,000–25,000</td>
<td>22,500</td>
<td>0.27</td>
<td>6075</td>
</tr>
<tr>
<td>25,000–30,000</td>
<td>27,500</td>
<td>0.20</td>
<td>5500</td>
</tr>
<tr>
<td>30,000–35,000</td>
<td>32,500</td>
<td>0.08</td>
<td>2600</td>
</tr>
<tr>
<td>35,000–40,000</td>
<td>37,500</td>
<td>0.02</td>
<td>750</td>
</tr>
</tbody>
</table>

\[\overline{M}_n = 21,150\]

\[m = 2 \times (12.01 \text{ g/mol}) + 3 \times (1.01 \text{ g/mol}) + 35.45 \text{ g/mol} = 62.5 \text{ g/mol}\]

\[DP = \frac{\overline{M}_n}{m} = \frac{21.150 \text{ g/mol}}{62.5 \text{ g/mol}} = 338\]
Molecular shape

(a) 

(b) 

(c)
End to End Distance, $r$

Adapted from Fig. 14.6, *Callister 7e.*
Molecular Structures

• Covalent chain configurations and strength:

- Linear
- Branched
- Cross-Linked
- Network

Direction of increasing strength

Adapted from Fig. 14.7, Callister 7e.
Polymers – Molecular Shape

Conformation – Molecular orientation can be changed by rotation around the bonds
– note: no bond breaking needed

Adapted from Fig. 14.5, Callister 7e.
Polymers – Molecular Shape

Configurations – to change must break bonds

- Stereoisomerism

\[ \text{H}_2\text{C} = \text{C} - \text{H} \quad \rightarrow \quad \text{H} - \text{C} - \text{C} - \text{H} \quad \text{or} \quad \text{H} - \text{C} - \text{C} - \text{R} \]

\[ \text{C} - \text{C} \quad \text{A} - \text{C} - \text{E} \quad \text{D} - \text{B} \quad \text{mirror plane} \]
Tacticity

**Tacticity** – stereoregularity of chain

- **isotactic** – all \( R \) groups on same side of chain
- **syndiotactic** – \( R \) groups alternate sides
- **atactic** – \( R \) groups random
cis/trans Isomerism

cis

cis-isoprene
(natural rubber)
bulky groups on same side of chain

trans

trans-isoprene
(gutta percha)
bulky groups on opposite sides of chain
Copolymers

two or more monomers polymerized together

- **random** – A and B randomly vary in chain
- **alternating** – A and B alternate in polymer chain
- **block** – large blocks of A alternate with large blocks of B
- **graft** – chains of B grafted on to A backbone
Polymer Crystallinity

Ex: polyethylene unit cell

- Crystals must contain the polymer chains in some way
  - Chain folded structure

Adapted from Fig. 14.10, Callister 7e.

Adapted from Fig. 14.12, Callister 7e.
Polymer Crystallinity

Polymers rarely 100% crystalline
• Too difficult to get all those chains aligned

• % Crystallinity: % of material that is crystalline.
  -- $T_S$ and $E$ often increase with % crystallinity.
  -- Annealing causes crystalline regions to grow. % crystallinity increases.

Adapted from Fig. 14.11, 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.)
Crystallinity

\[\text{crystallinity}\% = \frac{\rho_c (\rho_s - \rho_a)}{\rho_s (\rho_c - \rho_a)} \times 100\]

\(\rho_s\): density of sample
\(\rho_a\): density of totally amorphous polymer
\(\rho_c\): density of perfectly crystalline polymer
Polymer Crystal Forms

- Single crystals – only if slow careful growth
Polymer Crystal Forms

- **Spherulites** – fast growth – forms lamellar (layered) structures

Adapted from Fig. 14.13, *Callister 7e.*
Spherulites – crossed polarizers

Maltese cross
Defects in polymers

- Screw dislocation (ramp continues to spiral upward)
- Crystallite boundary
- Dangling chain
- Noncrystalline region
- Impurity
- Vacancy
- Edge dislocation (extra plane)
- Branch
- Chain ends
- Loose chain
Homework

14.3
14.6
14.19
14.26