Chapter 14: 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?
Ancient Polymers

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

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

Most polymers are hydrocarbons (made up of H and C)

Note: polyethylene is a long-chain hydrocarbon
- paraffin wax for candles is short polyethylene
Polymer Composition

Saturated hydrocarbons
Each carbon singly bonded to four other atoms
Example: Ethane, $\text{C}_2\text{H}_6$ or $\text{C}_n\text{H}_{2n+2}$

Unsaturated hydrocarbons
Double & triple bonds somewhat unstable – can form new bonds
- **Double bond** found in ethylene or ethene - $\text{C}_2\text{H}_4$ or $\text{C}_n\text{H}_{2n}$
- **Triple bond** found in acetylene or ethyne - $\text{C}_2\text{H}_2$ or $\text{C}_n\text{H}_{2n-2}$
# Table 14.1  Compositions and Molecular Structures for Some of the Paraffin Compounds: \( \text{C}_n\text{H}_{2n+2} \)

<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>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></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>
Isomerism

- Isomerism
  - two compounds with same chemical formula can have quite different structures
  
  for example: $\text{C}_8\text{H}_{18}$
  - normal-octane

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

  \[
  \downarrow
  \]

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

  - 2,4-dimethylhexane

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

  \[
  \text{CH}_2
  \]

  \[
  \text{CH}_3
  \]
Chemistry of polymer molecules

• Free radical polymerization  \( R = \text{CH}_3, \text{CH}_2\text{H}_5, \text{C}_6\text{H}_5 \ldots \)

\[
\text{free radical} + \text{monomer (ethylene)} \rightarrow \text{initiation}
\]

\[
\text{dimer} \rightarrow \text{propagation}
\]

• Initiator: example - benzoyl peroxide

\[
\text{benzoyl peroxide} \rightarrow 2 \text{ benzoyl radicals}
\]

Chapter 14 - 7
# 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>[\text{H} - \text{C} - \text{H} ]</td>
</tr>
<tr>
<td>Poly(vinyl chloride) (PVC)</td>
<td>[\text{H} - \text{C} - \text{H} ]</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>
<tr>
<td>Polystyrene (PS)</td>
<td>[\text{H} - \text{C} - \text{C} ]</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**

Number average molecular weight

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

\( x_i \) = number fraction of chains in size range \( i \)

\( M_i \) = mean (middle) molecular weight of size range \( i \)

Weight average molecular weight

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

\( w_i \) = weight fraction of chains in size range \( i \)

Adapted from Fig. 14.4, *Callister & Rethwisch 8e.*
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?
Molecular Weight Calculation (cont.)

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 $N_i$</th>
<th>mean number weight $W_i$</th>
<th>mean weight fraction $x_i$</th>
<th>total weight fraction $w_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>81-120</td>
<td>2</td>
<td>110</td>
<td>$\frac{2}{10} = 0.2$</td>
<td>$\frac{2 \times 110}{1881} = 0.117$</td>
</tr>
<tr>
<td>121-160</td>
<td>2</td>
<td>142</td>
<td></td>
<td></td>
</tr>
<tr>
<td>161-200</td>
<td>3</td>
<td>184</td>
<td></td>
<td></td>
</tr>
<tr>
<td>201-240</td>
<td>2</td>
<td>223</td>
<td></td>
<td></td>
</tr>
<tr>
<td>241-280</td>
<td>0</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>281-320</td>
<td>0</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>321-360</td>
<td>0</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>361-400</td>
<td>1</td>
<td>380</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

$$x_i = \frac{N_i}{\sum N_i} \quad w_i = \frac{N_i W_i}{\sum N_i W_i}$$

For example: for the 81-120 lb range

$$x_{81-120} = \frac{2}{10} = 0.2$$

$$w_{81-120} = \frac{2 \times 110}{1881} = 0.117$$
**Molecular Weight Calculation (cont.)**

<table>
<thead>
<tr>
<th>weight range</th>
<th>mean weight $W_i$</th>
<th>number fraction $x_i$</th>
<th>weight fraction $w_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>81-120</td>
<td>110</td>
<td>0.2</td>
<td>0.117</td>
</tr>
<tr>
<td>121-160</td>
<td>142</td>
<td>0.2</td>
<td>0.150</td>
</tr>
<tr>
<td>161-200</td>
<td>184</td>
<td>0.3</td>
<td>0.294</td>
</tr>
<tr>
<td>201-240</td>
<td>223</td>
<td>0.2</td>
<td>0.237</td>
</tr>
<tr>
<td>241-280</td>
<td>-</td>
<td>0</td>
<td>0.000</td>
</tr>
<tr>
<td>281-320</td>
<td>-</td>
<td>0</td>
<td>0.000</td>
</tr>
<tr>
<td>321-360</td>
<td>-</td>
<td>0</td>
<td>0.000</td>
</tr>
<tr>
<td>361-400</td>
<td>380</td>
<td>0.1</td>
<td>0.202</td>
</tr>
</tbody>
</table>

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

\[
\overline{M_w} = \sum w_i M_i = (0.117 \times 110 + 0.150 \times 142 + 0.294 \times 184 + 0.237 \times 223 + 0.202 \times 380) = 218 \text{ lb}
\]
Degree of Polymerization, $DP$

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

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

$DP = 6$

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

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

for copolymers this is calculated as follows:

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

Chain fraction $f_i$ mol. wt of repeat unit $i$
Molecular Structure and shape for Polymers

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. 14.5, Callister & Rethwisch 8e.
Molecular Configurations for Polymers: 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

**Atactic** — $R$ groups randomly positioned
Geometrical isomer
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
Molecular characteristics

- Chemistry
- Size
- Shape
- Structure

Isomeric states

- Linear
- Branched
- Crosslinked
- Network

Stereoisomers

- Isostactic
- Syndiotactic
- Atactic

Geometrical isomers

- cis
- trans
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 — B —
Polymer Crystallinity

- Crystalitte (small crystalline region)
- Chain folded structure

- Spherulite (semicrystalline)

Alternating chain-folded crystallites and amorphous regions
Spherulite structure for relatively rapid growth rates
Polymer Crystallinity (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.

Adapted from Fig. 14.11, *Callister 6e.*
Chapter 15: Characteristics, Applications & Processing of Polymers

ISSUES TO ADDRESS...

• What are the tensile properties of polymers and how are they affected by basic microstructural features?

• Hardening, anisotropy, and annealing in polymers.

• How does the elevated temperature mechanical response of polymers compare to ceramics and metals?

• What are the primary polymer processing methods?
Mechanical Properties of Polymers – Stress-Strain Behavior

Brittle polymer (crosslinked, network polymers)

Fibrillar structure

Plastic (semicrystalline polymers)

Elastomer

Underformed structure

Amorphous regions elongate

Crystalline region align

Crystalline block segments separate

Elastic moduli – less than for metals

Adapted from Fig. 15.1, Callister & Rethwisch 8e.

Chapter 14 - 22
Predeformation by Drawing

- **Drawing**...(ex: monofilament fishline)
  -- stretches the polymer prior to use
  -- aligns chains in the stretching direction
- Results of drawing:
  -- increases the elastic modulus ($E$) in the stretching direction
  -- increases the tensile strength ($TS$) in the stretching direction
  -- decreases ductility (%$EL$)
- **Annealing** after drawing...
  -- decreases chain alignment
  -- reverses effects of drawing (reduces $E$ and $TS$, enhances %$EL$)
- Contrast to effects of **cold working** in metals!

Adapted from Fig. 15.13, *Callister & Rethwisch 8e*. (Fig. 15.13 is from J.M. Schultz, *Polymer Materials Science*, Prentice-Hall, Inc., 1974, pp. 500-501.)
Mechanisms of Deformation—Elastomers

- Compare elastic behavior of elastomers with the:
  - brittle behavior (of aligned, crosslinked & network polymers), and
  - plastic behavior (of semicrystalline polymers)
  (as shown on previous slides)
Time-Dependent Deformation

- **Stress relaxation test:**
  - strain in tension to $\varepsilon_o$ and hold.
  - observe decrease in stress with time.

- **Relaxation modulus:**
  \[ E_r(t) = \frac{\sigma(t)}{\varepsilon_o} \]

- **There is a large decrease in $E_r$ for $T > T_g$.**

(adapted from Fig. 15.7, *Callister & Rethwisch 8e.*
(Fig. 15.7 is from A.V. Tobolsky, *Properties and Structures of Polymers*, John Wiley and Sons, Inc., 1960.)

Chapter 14 - 25
Time-Dependent Deformation

- Creep test:
  -- stress $\sigma_0$ is apply and hold.
  -- observe the strain evolution with time

- Creep modulus:

\[
E_c(t) = \frac{\sigma_0}{\varepsilon(t)}
\]

Many material can be subject to time dependant deformation when the stress level is maintained constant.

Viscoelastic creep can be really important even at room temperature. (example tires may develop flat spots if they parked for prolonged time period)
Crazing During Fracture of Thermoplastic Polymers

Craze formation prior to cracking

– during crazing, plastic deformation of spherulites
– and formation of microvoids and fibrillar bridges

Adapted from Fig. 15.9, *Callister & Rethwisch 8e.*
Thermoplastic/Thermosetting

Classification of polymers according to their behavior with rising the temperature

• Thermoplastic polymer soften when you rise the temperature (eventually liquefy) and harden when you cooled reversible irreversible if molten and raised at too high temperature. (little crosslinking, ductile, soften w/heating, polyethylene, polypropylene, polycarbonate, polystyrene.)

• Thermosetting (network polymers) they become permanently hard during their formation and don’t soften during heating bonds (network or cross linked) will resist to the vibration and rotation induced by the temperature. Thermosetting material are harder and stronger than thermoplastic. (significant crosslinking, 10 to 50% of repeat units, hard and brittle, do NOT soften w/heating, vulcanized rubber, epoxies, polyester resin, phenolic resin.)
Influence of $T$ and Strain Rate on Thermoplastics

- Decreasing $T$:  
  - increases $E$  
  - increases $TS$  
  - decreases $\%EL$

- Increasing strain rate:  
  - same effects as decreasing $T$.  

Adapted from Fig. 15.3, Callister & Rethwisch 8e. (Fig. 15.3 is from T.S. Carswell and J.K. Nason, "Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics", Symposium on Plastics, American Society for Testing and Materials, Philadelphia, PA, 1944.)
Melting & Glass Transition Temps.

What factors affect \( T_m \) and \( T_g \)?

- Both \( T_m \) and \( T_g \) increase with increasing chain stiffness.
- Chain stiffness increased by presence of:
  1. Bulky sidegroups
  2. Polar groups or sidegroups
  3. Chain double bonds and aromatic chain groups
- Regularity of repeat unit arrangements – affects \( T_m \) only

Adapted from Fig. 15.18, Callister & Rethwisch 8e.
Polymer Formation

- There are two types of polymerization
  - Addition (or chain) polymerization
  - Condensation (step) polymerization
Addition (Chain) Polymerization

- **Initiation**
  \[ R^- + \text{C} = \text{C} \xrightarrow{} \text{R} \text{C} = \text{C}^- \]

- **Propagation**
  \[ \text{R} \text{C} = \text{C}^- + \text{C} = \text{C} \xrightarrow{} \text{R} \text{C} \text{C} = \text{C}^- \]

- **Termination**
  \[ \text{R} \text{C} = \text{C} = \text{C}^- + \cdot \text{C} = \text{C} = \text{C}^- \xrightarrow{} \]

- Disproportionation
  \[ \text{R} \text{C} = \text{C} = \text{C}^- + \text{C} = \text{C} = \text{C}^- \xrightarrow{} \]

- Combination
  \[ \text{R} \text{C} = \text{C} = \text{C}^- + \text{C} = \text{C} = \text{C}^- \xrightarrow{} \]
Condensation (Step) Polymerization

\[
\text{hexamethylene diamine} \quad \text{adipic acid} \\
H_2N-(CH_2)_6N-H + HO-C-(CH_2)_4-C-OH \rightarrow \\
H_2N-(CH_2)_6N-C-(CH_2)_4-C-OH + H_2O
\]

nylon-6,6
Polymer Additives

Improve mechanical properties, processability, durability, etc.

- **Fillers**
  - Added to improve tensile strength & abrasion resistance, toughness & decrease cost
  - ex: carbon black, silica gel, wood flour, glass, limestone, talc, etc.

- **Plasticizers**
  - Added to reduce the glass transition temperature $T_g$ below room temperature
  - Presence of plasticizer transforms brittle polymer to a ductile one
  - Commonly added to PVC - otherwise it is brittle
Polymer Additives (cont.)

- **Stabilizers**
  - Antioxidants
  - UV protectants
- **Lubricants**
  - Added to allow easier processing
  - polymer “slides” through dies easier
  - ex: sodium stearate
- **Colorants**
  - Dyes and pigments
- **Flame Retardants**
  - Substances containing chlorine, fluorine, and boron
Processing Plastics – Compression Molding

Thermoplastics and thermosets
- polymer and additives placed in mold cavity
- mold heated and pressure applied
- fluid polymer assumes shape of mold

Fig. 15.23, Callister & Rethwisch 8e. (Fig. 15.23 is from F.W. Billmeyer, Jr., Textbook of Polymer Science, 3rd ed., John Wiley & Sons, 1984.)
Processing Plastics – Injection Molding

Thermoplastics and some thermosets

- when ram retracts, plastic pellets drop from hopper into barrel
- ram forces plastic into the heating chamber (around the spreader) where the plastic melts as it moves forward
- molten plastic is forced under pressure (injected) into the mold cavity where it assumes the shape of the mold

![Diagram of injection molding process]

Fig. 15.24, Callister & Rethwisch 8e. (Fig. 15.24 is from F.W. Billmeyer, Jr., Textbook of Polymer Science, 2nd edition, John Wiley & Sons, 1971.)
Processing Plastics – Extrusion

thermoplastics

- plastic pellets drop from hopper onto the turning screw
- plastic pellets melt as the turning screw pushes them forward by the heaters
- molten polymer is forced under pressure through the shaping die to form the final product (extrudate)

Fig. 15.25, Callister & Rethwisch 8e. (Fig. 15.25 is from Encyclopædia Britannica, 1997.)
Processing Plastics – Blown-Film Extrusion

Fig. 15.26, Callister & Rethwisch 8e.
(Fig. 15.26 is from Encyclopædia Britannica, 1997.)
Polymer Types – Fibers

Fibers - length/diameter >100

• Primary use is in textiles.
• Fiber characteristics:
  – high tensile strengths
  – high degrees of crystallinity
  – structures containing polar groups
• Formed by spinning
  – extrude polymer through a spinneret (a die containing many small orifices)
  – the spun fibers are drawn under tension
  – leads to highly aligned chains - fibrillar structure
Polymer Types – Miscellaneous

- **Coatings** – thin polymer films applied to surfaces – i.e., paints, varnishes
  - protects from corrosion/degradation
  - decorative – improves appearance
  - can provide electrical insulation

- **Adhesives** – bonds two solid materials (adherands)
  - bonding types:
    1. Secondary – van der Waals forces
    2. Mechanical – penetration into pores/crevices

- **Films** – produced by blown film extrusion

- **Foams** – gas bubbles incorporated into plastic
Summary

• Limitations of polymers:
  -- $E$, $\sigma_y$, $K_c$, $T_{\text{application}}$ are generally small.
  -- Deformation is often time and temperature dependent.

• Thermoplastics (PE, PS, PP, PC):
  -- Smaller $E$, $\sigma_y$, $T_{\text{application}}$
  -- Larger $K_c$
  -- Easier to form and recycle

• Elastomers (rubber):
  -- Large reversible strains!

• Thermosets (epoxies, polyesters):
  -- Larger $E$, $\sigma_y$, $T_{\text{application}}$
  -- Smaller $K_c$

Table 15.3 Callister & Rethwisch 8e:
Good overview of applications and trade names of polymers.
Summary

• Polymer Processing
  -- compression and injection molding, extrusion, blown film extrusion
• Polymer melting and glass transition temperatures
• Polymer applications
  -- elastomers  -- fibers
  -- coatings    -- adhesives
  -- films      -- foams
  -- advanced polymeric materials
Advanced Polymers

Ultrahigh Molecular Weight Polyethylene (UHMWPE)

- Molecular weight ca. $4 \times 10^6 \text{ g/mol}$
- Outstanding properties
  - high impact strength
  - resistance to wear/abrasion
  - low coefficient of friction
  - self-lubricating surface
- Important applications
  - bullet-proof vests
  - golf ball covers
  - hip implants (acetabular cup)

Adapted from chapter-opening photograph, Chapter 22, Callister 7e.