PHYSICAL PROPERTIES of POLYMERS

• Recognize the general physical characteristics that distinguish polymers from small molecules.
• Demonstrate an understanding of the factors that give rise to these characteristics: the structure of the polymer chain and the interactions of the polymer chain with its surroundings.
• Describe the nature of the transitions occurring at $T_g$ and $T_m$.
• Describe the significance of polymer solution properties, including colligative effects and solution viscosity.

Introduction

• General physical characteristics:
  – Polymers vary in form from viscous liquids (oligomers) to brittle, rubbery, or gummy solids
  – Solid polymers can be amorphous (glassy), crystalline, or both
  – Polymer properties may change with physical stress (stretching, compression)
  – Polymer solutions are viscous, even at low solute concentrations
• Polymer properties result from the large number of interparticle interactions the polymer chain has with its surroundings:
  – Internal associations among polymer chain substituents
  – Interactions between polymer chains
  – Interactions between polymer chains and solvent molecules
  – Interactions between polymer chains and additives
Polymer Molecule Size & Shape

- Polymer chain interactions depend on the shape of the molecule.
- Influencing factors:
  - Chemical structure
  - Chain length
  - Nearby molecules (other polymer chains, solvent, additives)

REVIEW: Interparticle Forces

- The physical properties of a material depend on its physical state.
- The physical properties of condensed phases (solids and liquids) depend on particle-particle interactions.
  - Intramolecular (bonding)
  - Intermolecular (non-bonding, interparticle)
- Bonding forces are relatively strong.
  - Charges operating at short distances
- Non-bonding forces are relatively weak.
  - Low-strength charges operating at greater distances
Comparison of Bonding Forces

<table>
<thead>
<tr>
<th>Force</th>
<th>Basis of Attraction</th>
<th>Energy, kJ/mol</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic</td>
<td>Cation ↔ Anion</td>
<td>400-4000</td>
<td>NaCl</td>
</tr>
<tr>
<td>Covalent</td>
<td>Nuclei ↔ Shared e⁻ pair</td>
<td>15-1100</td>
<td>H₂</td>
</tr>
<tr>
<td>Metallic</td>
<td>Cation ↔ Delocalized e⁻</td>
<td>75-1000</td>
<td>Hg</td>
</tr>
</tbody>
</table>
Comparison of Nonbonding Forces

<table>
<thead>
<tr>
<th>Force</th>
<th>Basis of Attraction</th>
<th>Energy, kJ/mol</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion-Dipole</td>
<td>Ion charge ↔ Dipole charge</td>
<td>40–600</td>
<td>Na⁺ ··· OH₂</td>
</tr>
<tr>
<td>H bond</td>
<td>X-H bond ↔ Dipole charge</td>
<td>10–40</td>
<td>HO-H ··· OH₂</td>
</tr>
<tr>
<td>Dipole-Dipole</td>
<td>Dipole charge ↔ Dipole charge</td>
<td>5–25</td>
<td>I-Cl ··· I-Cl</td>
</tr>
<tr>
<td>Ion-Induced dipole</td>
<td>Ion charge ↔ Polarizable e⁻ cloud</td>
<td>3–15</td>
<td>Fe²⁺ ··· O₂</td>
</tr>
<tr>
<td>Dipole-Induced dipole</td>
<td>Dipole charge ↔ Polarizable e⁻ cloud</td>
<td>2–10</td>
<td>H₂O ··· I-I</td>
</tr>
<tr>
<td>Dispersion</td>
<td>Polarizable e⁻ cloud ↔ Polarizable e⁻ cloud</td>
<td>0.05–40</td>
<td>Br-Br ··· Br-Br</td>
</tr>
</tbody>
</table>

Dipole Interactions

- Electrons that make up some bonds are not shared equally (ΔEN).
- Charged ends attract other charged species or species in which charges can be induced:

- These interactions, which depend on molecular size, can be moderately strong in certain cases.
Special Case: Hydrogen Bonding

- Bonds between H and electronegative elements (X = N, O, F, Cl) are particularly strong dipoles.

- The attraction between the H atom of one dipole and the X atom of another is called a HYDROGEN BOND.

Responsible for properties of H₂O, a molecule that, for its size, has relatively
- High surface tension
- High heat capacity, heat of vaporization
- Great solvent power
- Complex density profile (max at 4°C)

Dispersion Forces

- There is a small chance that the electrons in any bond will be unevenly distributed for a short period of time (instantaneous dipoles).

- A pure covalent bond would then gain dipole character and attract other temporary dipoles.

- The averages of many such weak, short-lived attractions are called dispersion forces (London or van der Waals forces).
• The magnitude of dispersion forces depends in molecular shape.

• Polarizability is a measure of how easy it is to distort a molecule’s charge distribution and produce short-lived attraction forces.

• Polarizability is a function of the number and types of bonds in a molecule. Larger molecules—such as polymers—have greater polarizabilities than small molecules.

• The magnitude of dispersion forces increases with molecular weight—this is why polymers have unique solution properties.

• Dispersion forces operate between all molecules.
Exercise

Identify the dominant attractive force in
a) NaCl(s)
b) CH₃CH₂CH₂CH₂CH₂(ℓ)
c) CH₃OH(aq)
d) CH₃COO⁻·Na⁺ (aq)

Polymer Chain Interactions: Overview

• Order (linearity, crystallinity, molecular weight distribution) affects properties,
  - Highly-ordered structure increases properties such as melting temperature and toughness,
  - Highly-ordered structure decreases properties such as flexibility.

• Short range order depends on composition, linearity, entanglements.

• Interactions between chains are always significant.
  - Interactions may be strong (dipole-dipole) or weak (dispersion forces), BUT
  - Long chains allow many interactions.
  - Attractions accumulate to very significant values.
**Linearity**

- **LDPE** (branched, lower density)
- **HDPE** (linear, higher density)

**Entanglements**

Chains must slide past each other by **reptation**

**Elastomeric properties**

**Ex:** NR undergoes stress-induced crystallization

- Stretch
- Relax

increased order

$\Delta S > 0$
$\Delta G < 0$

$\Rightarrow \Delta S < 0$
Transition Behavior

- Amorphous polymers change between a brittle or rigid glassy state — at lower $T$ — and a rubbery state. This transition occurs at a polymer’s glass transition temperature ($T_g$). Important in elastomers.

- Crystalline polymers change between a crystalline state — at lower $T$ — and a viscous fluid state. This transition occurs at a polymer’s melting temperature ($T_m$). Important in thermoplastics.

- Polymers with both amorphous and crystalline regions exhibit both transitions:
  - Amorphous regions undergo glass transition only.
  - Crystalline regions undergo melting only.

$T_m$: Influence of Structure

<table>
<thead>
<tr>
<th>Polyethylene Crystallinity, %</th>
<th>55</th>
<th>70</th>
<th>85</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_m$, °C</td>
<td>109</td>
<td>125</td>
<td>133</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>0.92</td>
<td>0.94</td>
<td>0.96</td>
</tr>
<tr>
<td>Yield stress, MPa</td>
<td>12</td>
<td>23</td>
<td>35</td>
</tr>
</tbody>
</table>
**$T_g$: Influence of Structure**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>-133</td>
</tr>
<tr>
<td>Polyisoprene</td>
<td>-72</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>64</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>79</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>95</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>105</td>
</tr>
<tr>
<td>Poly(2,6-diMe-1,4-phenylene oxide)</td>
<td>207</td>
</tr>
</tbody>
</table>


**$T_g$: Influence of Molecular Weight**

![Graph showing $T_g$ vs. $M$](image)

$T_g = T_{g,m} - \frac{K}{M_n}$

Adapted from A. Abou Elfadl et al. 2010 Macromolecules, 43, 3340-3351.
Example: Natural Polymer

H-Bonding and DNA Melting Temperature:

Examples: Synthetic Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>T_g, °C</th>
<th>T_m, °C</th>
<th>Tensile Str., MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-density Polyethylene</td>
<td>-125</td>
<td>105-120</td>
<td>12</td>
</tr>
<tr>
<td>High-density Polyethylene</td>
<td>-78</td>
<td>130-135</td>
<td>26-33</td>
</tr>
<tr>
<td>Nylon-6,6</td>
<td>50</td>
<td>255-265</td>
<td>45-75</td>
</tr>
</tbody>
</table>
Phase Transitions and Structure

$T_m$ and $T_g$ increase with

- Increasing intermolecular forces
- Increasing intra- and intermolecular barriers to chain rotation
- Bulky, stiff backbone and side groups
- Shorter flexible side groups

Adapted from R.F. Boyer, 1963 Rubber Chem. Technol. 36, 1303-1421;
Exercise

Which of the following polymers would most likely have the highest $T_g$?

a) A linear polyethylene with $M_w = 1,000,000$.

b) A branched polyethylene with $M_w = 1,000,000$.

c) A linear polyisoprene with $M_w = 1,000,000$.

d) A linear nylon-6,6 with $M_w = 1,000,000$. 

Solution properties

Polystyrene

Soluble in hydrocarbons

Polyacrylonitrile

Insoluble in hydrocarbons

Like dissolves like
For a freely jointed chain of \( n \) links, each of length \( \ell \), the root mean square (RMS) end-to-end distance is

\[
\langle r^2 \rangle^{1/2} = n^{1/2} \ell
\]

Properties of polymers in solution — including those with 0 or >2 chain ends — are a function of the radius of gyration, the RMS distance of chain links from the chain’s center of mass:

\[
\langle s^2 \rangle^{1/2} = \frac{\langle r^2 \rangle^{1/2}}{6^{1/2}}
\]

This gives us a way to think about the size of a polymer chain in solution.

Solution Process: Small Molecules

- Solvent molecules solvate the surface of the solute.
- Partially solvated molecules dissociate from the solute crystal.
- Solvation is completed as the fully solvated solute molecules diffuse into the solvent.
Solution Process: Polymers

- Solvent molecules penetrate the polymer phase; the polymer becomes swollen.
- The polymer chains solvate segment by segment until the entire molecule is solvated.
- The fully-solvated polymer molecules diffuse out of the polymer phase.

Solution Viscosity

- Viscosity is resistance to flow (N·s/m²).
- The net effect of chain interactions is that polymers tend to have high viscosities, both as melts or in solution.
- Viscosity depends on MW, [polymer], and the nature of the solvent.

Exercise

Which of the following polymer solutions would be the least viscous?

a) A 1% solution of polyisoprene in hexane.
b) A 2% solution of polyisoprene in pentane.
c) A 1% solution of polyisoprene in an 80:20 mixture of hexane and acetone.
d) A 2% solution of polyisoprene in an 80:20 mixture of hexane and acetone.

Colligative Properties

Properties that depend on the number of solute particles

- Depend on how many solute particles, but not their chemical structure or size
- Include:
  - Vapor pressure lowering \( (\Delta T/c)_{c=0} = K_{Rv}/M_n \)
  - Boiling point elevation \( (\Delta T/c)_{c=0} = K_b/M_n \)
  - Freezing point depression \( (\Delta T/c)_{c=0} = K_f/M_n \)
  - Osmotic pressure \( (\Pi/c)_{c=0} = RT/M_n \)
**Vapor Pressure Lowering**

Small molecules:
Solution vapor pressure decreases in proportion to the concentration of solute (Raoult’s Law):

\[ \Delta P = \chi_{solute} \times P^o_{solvent} \]

**Osmosis**

Diffusion of a solvent through a **semipermeable membrane** from a more dilute solution to a more concentrated one

Semipermeable membrane: small molecules (such as solvent) go through, large molecules (such as polymers) do not

**RESULT:** PRESSURE due to one-way solvent flow
• Solvent flows “uphill” until pressure equalized
• Osmotic pressure : Pressure required to stop osmosis
Examples:

<table>
<thead>
<tr>
<th>$M$</th>
<th>$\Pi$, torr*</th>
<th>$-\Delta P_{\text{vap}}^*$, torr</th>
<th>$+\Delta T_s^*$, °C</th>
<th>$-\Delta T_f^*$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>——</td>
<td>0.736</td>
<td>0.253</td>
<td>0.490</td>
</tr>
<tr>
<td>10,000</td>
<td>288</td>
<td>$799 \times 10^{-5}$</td>
<td>$272 \times 10^{-5}$</td>
<td>$577 \times 10^{-5}$</td>
</tr>
<tr>
<td>100,000</td>
<td>29</td>
<td>$80 \times 10^{-5}$</td>
<td>$27 \times 10^{-5}$</td>
<td>$58 \times 10^{-5}$</td>
</tr>
<tr>
<td>500,000</td>
<td>6</td>
<td>$16 \times 10^{-5}$</td>
<td>$5 \times 10^{-5}$</td>
<td>$12 \times 10^{-5}$</td>
</tr>
<tr>
<td>1,000,000</td>
<td>3</td>
<td>$8 \times 10^{-5}$</td>
<td>$3 \times 10^{-5}$</td>
<td>$6 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

*solute = 10 g/dm³ in benzene.

Why Are Solution Properties Important?

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Effect</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM</td>
<td>Gasoline</td>
<td>Improves ply-to-ply bonding</td>
<td>Roofing</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>Poly(vinylidene fluoride)</td>
<td>Increases oil, solvent resistance</td>
<td>Automobile, truck components</td>
</tr>
<tr>
<td>Poly(vinyl polypyrrolidone)</td>
<td>Wine, beer</td>
<td>Forms gel with tannin impurities</td>
<td>Beverage clarification</td>
</tr>
<tr>
<td>Poly(ethylene oxide)</td>
<td>Water</td>
<td>Reduces turbulent flow</td>
<td>Heat exchange fluids</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>Diisononyl phthalate</td>
<td>Plasticizes polymer</td>
<td>Flexible PVC</td>
</tr>
<tr>
<td>Polysisoprene</td>
<td>Acetone-pentane azeotrope</td>
<td>Allows separation of high-MW polymer</td>
<td>High bulk viscosity guayule rubber (GR)</td>
</tr>
</tbody>
</table>

Adapted from L.H. Sperling, 1992 Introduction to Physical Polymer Science, 2nd Ed, p 123.
Exercise

The colligative properties of a polymer are determined by its

a) Number-average molecular weight.

b) Weight-average molecular weight.

c) Glass transition temperature.

d) Melting temperature.