Structure and Morphology

• Into what types of overall shapes or conformations can polymer chains arrange themselves?

• How do polymer chains interact with one another?

• Into what types of forms or morphologies do the chains organize?

• What is the relationship of conformation and morphology to polymer microstructure?

• What is the relationship of conformation and morphology to macroscopic properties.
States of Matter

Usually consider;

- **Solids**
- **Liquids**
- **Gases**
Polymers

More complex behaviour

Temperature

No Gaseous State

Viscoelastic liquid

Glassy Solid

Crystallization

Melting

Semicrystalline Solid

Glass Transition
States of Matter

Small Molecules

“1st-Order” Transitions

Solid

Liquid

Gas

Small Molecules

Gas

Liquid

Solid (Crystalline)

Volume

Temperature $T_c$

Cool

Solid

Liquid

Gas
Crystallizable materials can form metastable glasses. What about polymers like atactic polystyrene that cannot crystallize?

Observed Behavior depends on:

- Structure
- Cooling Rate
- Crystallization Kinetics

Crystallizable materials can form metastable glasses.

*What about polymers like atactic polystyrene that cannot crystallize?*
Polymer Structure

The Issues

• Bonding & the Forces between Chains
• Conformations
  • Ordered
  • Disordered
• Stacking or Arrangement of Chains in Crystalline Domains
• Morphology of Polymer Crystals
Bonding and Intermolecular Interactions

What are the forces between chains that provide cohesion in the solid state?

What determines how close these chains pack?
<table>
<thead>
<tr>
<th>Type of Interaction</th>
<th>Characteristics</th>
<th>Approximate Strength</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersion Forces</td>
<td>Short Range Varies as $-1/r^6$</td>
<td>About 0.2 - 0.5 kcal/mole</td>
<td>Poly(ethylene) Poly(styrene) (simple hydrocarbon polymers)</td>
</tr>
<tr>
<td>Dipole/dipole Interactions (Freely Rotating)</td>
<td>Short Range Varies as $-1/r^6$</td>
<td>About 0.5 - 2 kcal/mole</td>
<td>Poly(acrylonitrile) PVC</td>
</tr>
<tr>
<td>Strong Polar Interactions and Hydrogen Bonds</td>
<td>Complex Form but also Short Range</td>
<td>About 1 - 10 kcal/mole</td>
<td>Nylons Poly(urethanes)</td>
</tr>
<tr>
<td>Coulombic Interactions (Ionomers)</td>
<td>Long Range Varies as 1/r</td>
<td>About 10 - 20 kcal/mole</td>
<td>Surlyn</td>
</tr>
</tbody>
</table>

**Increasing Interaction Strength**
Conformations

Ordered

Disordered
Morphology

THE STUDY OF FORM AND STRUCTURE

Polymer morphology - the study of order within macromolecular solids

Our focus;

Morphology of semi-crystalline Polymers

Single crystal lamellae
Spherulites
Fibers
X-ray Diffraction

Diagram showing X-ray beam, single crystal, diffraction spots, photographic plate, crystalline powder, and diffraction rings.
X-ray Diffraction
X-ray Diffraction;
The n- Alkanes and Polyethylene
Polymers are Semicrystalline
Melting Temperatures

![Graph showing melting temperatures for different compounds.](image)
Crystallinity in Polymers

• CRISTALLINE MATERIALS
  – Either crystalline (~100 %, neglecting defects) or amorphous at a particular temperature
  – Melt at a sharp, well-defined temperature

• CRISTALLIZABLE POLYMERS
  – Never 100% Crystalline
  – Melt over a Range of Temperatures

"POLYMERS HAD LAID UPON THEM THE CURSE OF NOT OBEYING THERMODYNAMICS"

J.D.Hoffman,G.T.Davis,J.I.Lauritzen
In "Treatise on Solid State Chemistry"
N.B.Hannay,ed Vol 3, Ch7,Plenum Press
New York,1976
Questions

But now we can add to our list of questions, which have essentially become:

- **What is the Conformation of the Chains in the Crystalline Domains and how are they Stacked relative to one another?**

- **What is the Overall Shape and Form of the Crystals?**

- **What are the Relative Arrangements of the Crystalline and Amorphous Parts?**
The unit cell contains segments of different chains.

Chain Arrangements and Morphology

Are some chains entirely within the crystalline part while others are entirely within amorphous bits?

Do chains pass through both regions?
The Fringed Micelle Model

The First Really Useful Model
Single Crystal Lamellae


Courtesy of I.R. Harrison, Penn State
Polyethylene Single Crystals

85°C, 87°C, 90°C, 93°C, 95°C
Regular Chain Folding
The Flory Switchboard Model

Regular Folding Chain (Adjacent Re-entry)

Irregular Chain Folding (Random Re-entry)
The Flory Switchboard Model
Flory Strikes Back!

Spherulites
Spherulites

IPP Spherulite grown from a 10% IPP, 90% APP mixture

Structure of a spherulite
Fibers
Fibers
Fibers
What we would like
to get
<table>
<thead>
<tr>
<th>Property</th>
<th>Change with Increasing Degree of Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strength</td>
<td>Generally increases with degree of crystallinity</td>
</tr>
<tr>
<td>Stiffness</td>
<td>Generally increases with degree of crystallinity</td>
</tr>
<tr>
<td>Toughness</td>
<td>Generally decreases with degree of crystallinity</td>
</tr>
<tr>
<td>Optical Clarity</td>
<td>Generally decreases with increasing degree of crystallinity. Semi-crystalline polymers usually appear opaque</td>
</tr>
<tr>
<td></td>
<td>because of the difference in refractive index of the amorphous and crystalline domains, which leads to scattering. Will depend upon crystallite size.</td>
</tr>
<tr>
<td>Barrier Properties</td>
<td>Small molecules usually cannot penetrate or diffuse through the crystalline domains, hence “barrier properties”, which make a polymer useful for things like food wrap, increase with degree of crystallinity</td>
</tr>
<tr>
<td>Solubility</td>
<td>Similarly, solvent molecules cannot penetrate the crystalline domains, which must be melted before the polymer will dissolve. Solvent resistance increases with degree of crystallinity</td>
</tr>
</tbody>
</table>