Polymer "Solid" State

Semi-Crystalline  |  Amorphous

Glassy  |  Rubbery

Q: Relationship to Microstructure
Q: Relationship of Structure to Properties
Small Molecules

“1st-Order” Transitions

- Gas
- Liquid
- Solid (Crystalline)

Vol

\[ T_c \quad \text{(or } T_m) \quad \text{Temp} \]
Many Materials form metastable glasses - what about polymers like PET, atactic polystyrene?
States of Matter

No Gaseous State

Liquid State -- Viscoelastic Melt

- Cool
- Cool + X-link
- Cool

Semi-Crystalline Solid
Elastomer
“Semi-Solid” (like Silly Putty)
Glass

Also: x-linked rubber + solvent (gel)
liquid crystalline polymers, etc.
History of Rubber

~ 1500  Columbus Stumbles Across Haiti
~ 1600  Missionaries Observe Indians Making Crude Rubber Shoes (Caoutchouc)
1700  Joseph Priestly Invents a Name
1820  1st Rubber Shoes
1832  Mackintosh
1833  Goodyear Starts Work on Rubber
1844  Vulcanization
1875  Henry Wickham -- Pirate or Con-Man?
1922  Stevenson Plan
1942  Synthetic Rubber Project
1988  Penn State Rubber Project
Harrison Experiment

- Material Derived from Trojan-Enz
- Samples Cut Out With a Dog Bone Cutter
- Test -- Tensile Elongation (1 cm per minute)
- Uniaxial Deformation
  ~ 1,000 %
- Biaxial Deformation
  ~ 300 %
- Estimated Burst Pressure ~ 57 psi
  ~ 4 atm.
The Issues

- Bonding & the Forces between Chains
- Conformations
  - Ordered
  - Disordered
- Stacking or Arrangement of Chains in Crystalline Domains
- Morphology of Polymer Crystals (and Things like Block Copolymers)
# Interactions

Interaction Energy Depends Upon the Balance Between Attractive and Repulsive Forces

**Attractive Forces**

<table>
<thead>
<tr>
<th>Type of Interaction</th>
<th>Characteristics</th>
<th>Approximate Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersion Forces</td>
<td>Short Range</td>
<td>~0.2 to 2 kcal./mole</td>
</tr>
<tr>
<td>Dipole / dipole (Freely Rotating)</td>
<td>Varies as $1/r^6$</td>
<td></td>
</tr>
<tr>
<td>Strong Polar Forces &amp; Hydrogen Bonds</td>
<td>Complex Form, but Short Range</td>
<td>~ 1 to 10 kcal./mole</td>
</tr>
<tr>
<td>Coulombic, as Found in Ionomers</td>
<td>Long Range, Varies 1/r</td>
<td>~ 10 to 20 kcal/mole</td>
</tr>
</tbody>
</table>
Dispersion Forces

Interaction between fluctuating dipoles whose average value is zero (!)

eg: simple hydrocarbons
**Polar Forces**

Hydrogen Bonds

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**Chain-like Hydrogen Bonded Structures**

- Amide Groups
- Urethane Groups
- Hydroxyl Groups
Ionomers

Schematic Diagram of Clusters in an Ionomer.
Hydrocarbons -- PE, IPP, PS, etc.
  - Weak Dispersion Forces
Polar Polymers -- PVC, PAN, etc.
  - Eg: Those Containing Heteroatoms (O, N, Cl, F) -- Dipole/dipole Interactions
Hydrogen Bonding Polymers
  - Eg: Nylons, Polyurethanes, etc.
Ionomers
  - Eg: Surlyn