Crystalline Structures

Single Crystals

Polymer Spherulites

Physical State Transitions

Amorphous Polymer  Crystalline Polymer

Liquid  Liquid
Gum  Flexible Thermoplastic
Rubber
Glass

Increasing Temperature

$T_g$  $T_m$
Crystalline Structures

Spherulite Morphology

Folding and “Re-entry”

Youyong Li and William A. Goddard III

*Macromolecules* 2002 35 (22), 8440-8455
Crystallinity by DSC

- Experiment Setup

![Diagram of DSC setup with sample pan, polymer sample, reference pan, heaters, and computer to monitor temperature and regulate heat flow.](image)

Graph showing heat flow (mW) vs. temperature (°C) with peaks for glass transition, crystallization, and melting.
Crystallinity by DSC

Example: Crystallinity of Polyethylene

%Crystallinity = \frac{\Delta H_{\text{obs}}^f}{\Delta H_{\text{f}}^o} \times 100\%

Table: Heats of fusion of 100% crystalline polymers

<table>
<thead>
<tr>
<th>Acronym (f)</th>
<th>Name</th>
<th>Enthalpy (kJ/mol)</th>
<th>Repeat Unit</th>
<th>Molecular Weight (g/mol)</th>
<th>Enthalpy (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>Polyethylene</td>
<td>4.31</td>
<td>-CH₂</td>
<td>14.03</td>
<td>293</td>
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<tr>
<td>PP</td>
<td>Polypropylene</td>
<td>8.70</td>
<td>-CH₂(CH₂CH₃)</td>
<td>42.08</td>
<td>207</td>
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<td>PB</td>
<td>Polybutene-1</td>
<td>7.00</td>
<td>-CH₂(CH₂CH₃)</td>
<td>56.1</td>
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<td>POM</td>
<td>Polyoxymethylene</td>
<td>9.79</td>
<td>-CH₂O</td>
<td>30.03</td>
<td>328</td>
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<tr>
<td>PEON</td>
<td>Polypyrroleoxide</td>
<td>8.05</td>
<td>-CH₂OH</td>
<td>44.05</td>
<td>197</td>
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<tr>
<td>PA6</td>
<td>Polyacrylamide</td>
<td>26.0</td>
<td>-NH(CH₂)₂CO-</td>
<td>113.2</td>
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<tr>
<td>PA11</td>
<td>Polymaleic acid</td>
<td>44.7</td>
<td>-NH(CH₂)₂CO-</td>
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<tr>
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<td>PA66</td>
<td>Polyhexamethylene adipamide</td>
<td>57.8</td>
<td>-NH(CH₂)₂NHCO(CH₂)₂CO-</td>
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<td>226</td>
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<td>PA69</td>
<td>Polyhexamethylene sebacamide</td>
<td>69.1</td>
<td>-NH(CH₂)₂NHCO(CH₂)₂CO-</td>
<td>288.4</td>
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<td>PA610</td>
<td>Polyhexamethylene sebacamide</td>
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<td>-NH(CH₂)₂NHCO(CH₂)₂CO-</td>
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<td>PA612</td>
<td>Polyhexamethylene sebacamide</td>
<td>80.1</td>
<td>-NH(CH₂)₂NHCO(CH₂)₂CO-</td>
<td>310.1</td>
<td>258</td>
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<tr>
<td>PVC</td>
<td>Poly(vinyl chloride)</td>
<td>4.30</td>
<td>-CH₂Cl</td>
<td>59.0</td>
<td>82.0</td>
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<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
<td>5.44</td>
<td>-CH₂(CF₂)₂</td>
<td>82.0</td>
<td>66.3</td>
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<td>PTFE</td>
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<td>PVDF</td>
<td>Poly(vinylidene fluoride)</td>
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<td>-CH(CF₂)</td>
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<td>66.3</td>
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<td>PEEK</td>
<td>Polyetheretherketone</td>
<td>5.87</td>
<td>-CH₂OC(OH)₂OC₂H₄O-</td>
<td>288.3</td>
<td>130</td>
</tr>
</tbody>
</table>
Dilatometry

*Dilation* or change in specific volume

Liquid of known density and thermal expansion coefficient

Polymer

Computing crystallinity

\[
\%C = \frac{v_{\text{amorphous}} - v_{\text{partially crystalline}}}{v_{\text{amorphous}} - v_{\text{totally crystalline}}}
\]
Dilatometry

- Example: Nylon
- How would you find the density (i.e. specific volume) of this crystal given the size and shape?

\[
\% C = \frac{V_{\text{amorphous}} - V_{\text{partially crystalline}}}{V_{\text{amorphous}} - V_{\text{totally crystalline}}}
\]

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Macromolecules 2002 35 (22), 8440-8455
Wide angle x-ray scattering/diffraction

- **X-rays**: light with wavelength $\sim 0.1$-10Å – the same length scale as interatomic distances
- **Diffraction occurs only at specific angles**, given by the Bragg eqn.

$$n\lambda = 2d \sin \theta$$
\[ n\lambda = 2d \sin \theta \]
Wide angle x-ray scattering/diffraction

Why $2\theta$?

Diagram showing a diagram of an x-ray scattering setup with labels for beam catcher, detector, direct beam, screw to tighten height adjustment, lateral adjustment, arc adjustment, and x-ray beam. There is also an image of a diffraction pattern.
What if it’s not a single crystal?

- Polycrystalline samples look different.
- Example: Highly crystalline polymer with (mostly) oriented crystallites.
- Diffraction spots are blurred into lines.
What if it’s not a single crystal?

- Polycrystalline samples look different.
- Example: Highly crystalline polymer with no orientation of crystallites.
- Diffraction spots are blurred into full circles.
What if it’s not crystalline?

- Diffraction circles become much less defined and blurred.
- Sharpness of circles gives a clue to crystallinity.
An estimate of crystallinity

- The crystallinity can be estimated by comparing the areas of the peaks due to the amorphous polymer with those of the crystalline phase:

\[ \%C = \frac{A_{cr}}{(A_{cr} + A_{am})} \]
Example: Strain-induced Crystallization

S. Toki et al. / Polymer 41 (2000) 5423–5429
Other methods: IR & NMR

Ying Zheng, Merlin L. Bruening, and, Gregory L. Baker
Macromolecules 2007 40 (23), 8212-8219
**Conclusion: A comparison**

<table>
<thead>
<tr>
<th>Method of Analysis</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Differential Scanning Calorimetry</td>
<td>Fast, easy; You’re probably going to use DSC anyway for T&lt;sub&gt;g&lt;/sub&gt;, etc.</td>
<td>Need literature values of heat of fusion for 100% crystalline polymer for comparison; thermal history an issue.</td>
</tr>
<tr>
<td>Dilatometry</td>
<td>A simple way to measure polymer crystallinity based on changes in volume.</td>
<td>Pure crystalline specific volume must be known.</td>
</tr>
<tr>
<td>X-ray scattering</td>
<td>Can determine precise crystal structure.</td>
<td>Difficult to analyze data, determine structure.</td>
</tr>
<tr>
<td>Polarized Optical Microscopy</td>
<td>A quick way to see if a polymer is crystalline.</td>
<td>Other factors (like strain in the polymer) can cause birefringence; difficult to quantify.</td>
</tr>
</tbody>
</table>
Conclusion

- Offshoot: A combination of methods may be the best solution (e.g. x-ray scattering, DSC)
- Polymer crystallinity contributes to the strength of many polymeric materials.
- Questions?