# Crystallinity in Polymers

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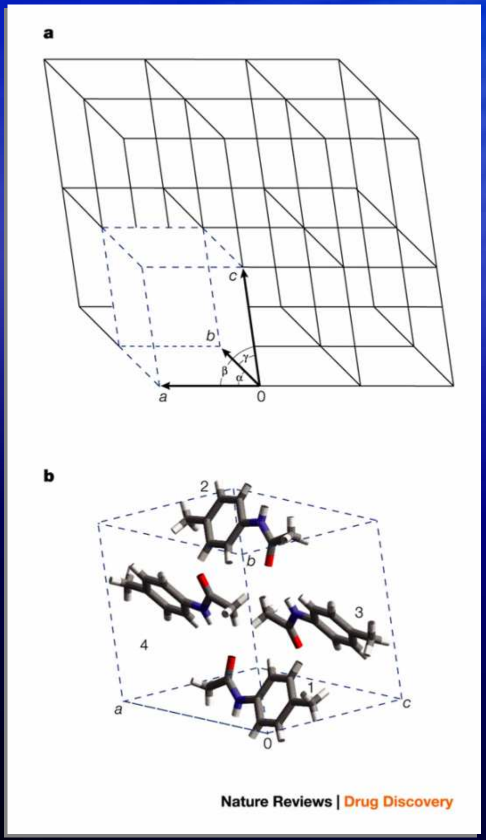
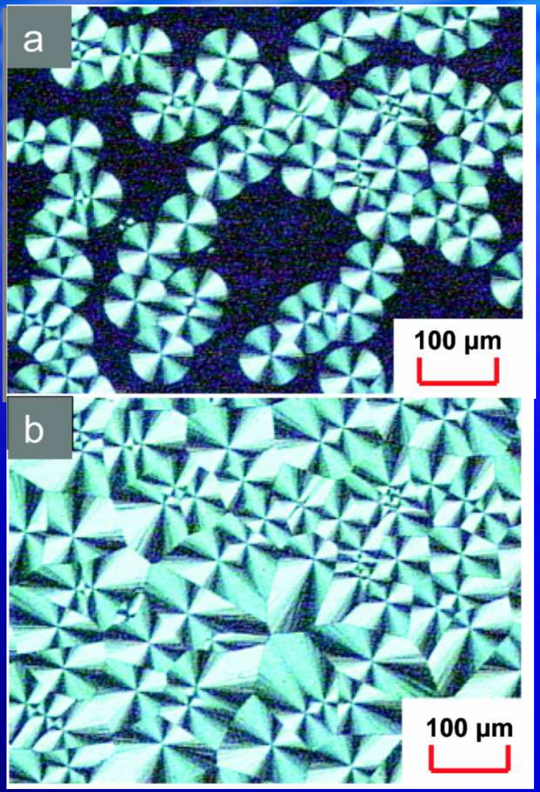
February 12, 2009

# Crystalline Structures

## Single Crystals

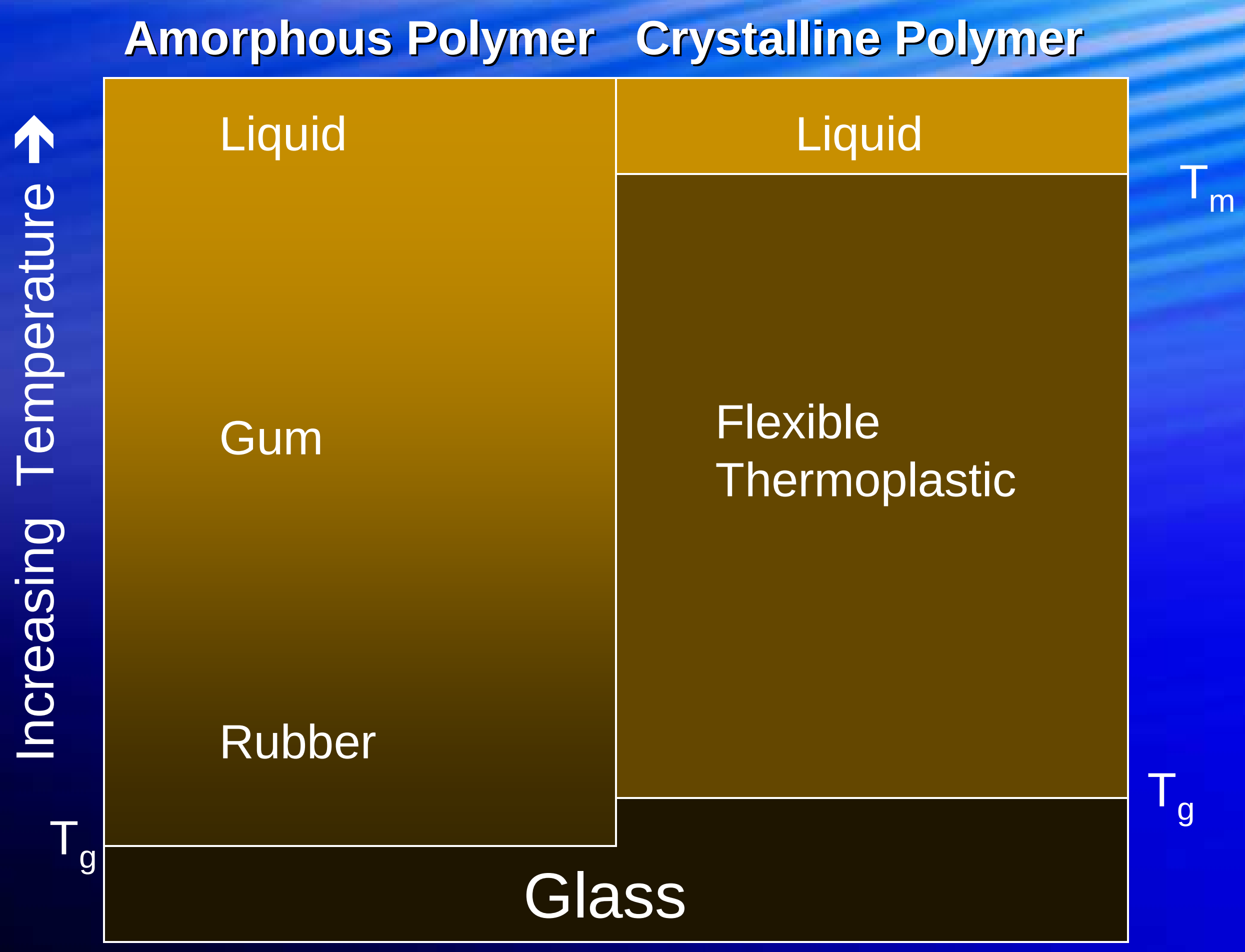



## Polymer Spherulites




Sharmistha Datta & David J. W. Grant, *Nature Reviews Drug Discovery* 3, 42-57 (January 2004)

# Physical State Transitions



# Crystalline Structures

## Spherulite Morphology

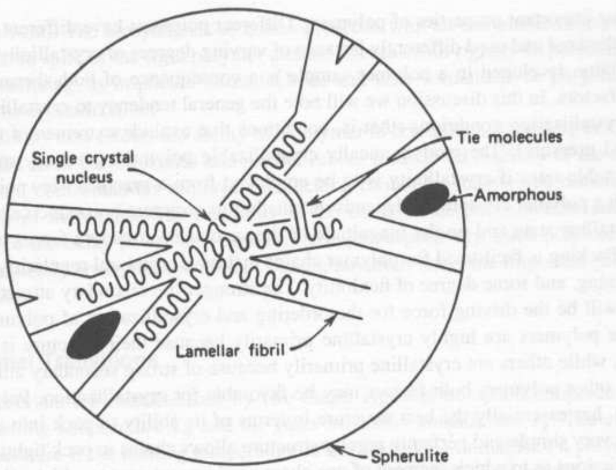
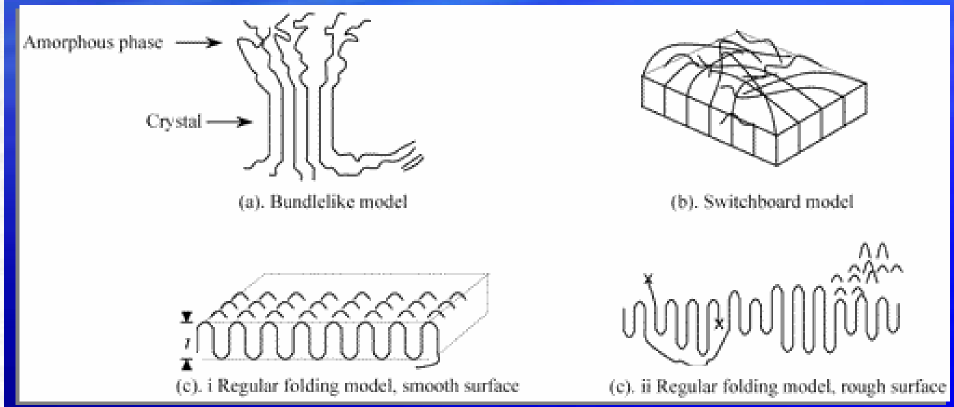



Fig. 1-8 Structural organization within a spherulite in melt-crystallized polymer.

(from Odian)

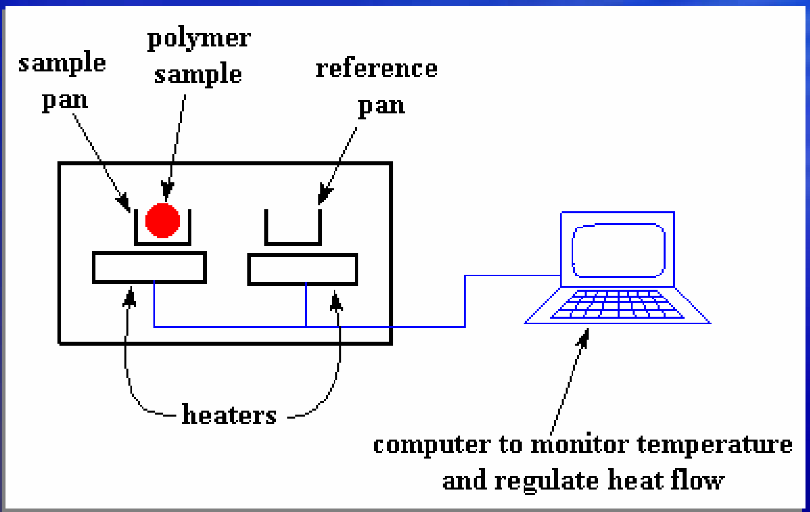
## Folding and "Re-entry"

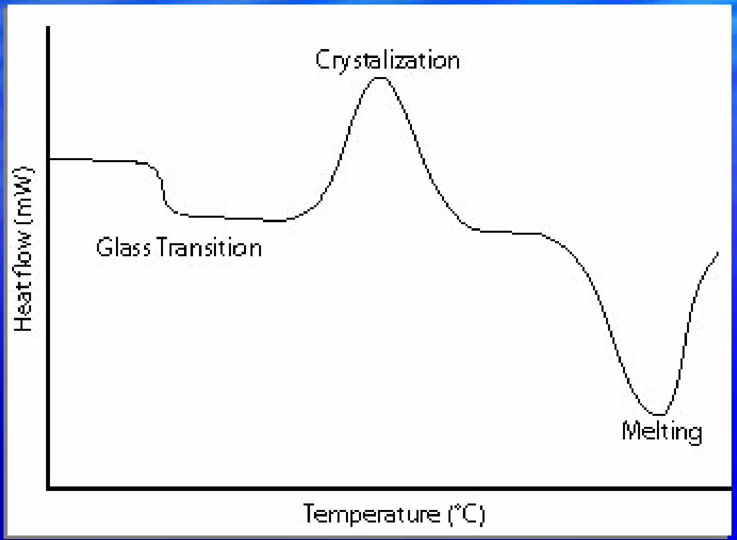



**Youyong Li and William A. Goddard III**
***Macromolecules*** **2002 35 (22), 8440-8455**

# Crystallinity by DSC

- Experiment Setup



# Crystallinity by DSC

- Example: Crystallinity of Polyethylene

$$\%Crystallinity = \frac{\Delta H_f^{obs}}{\Delta H_f^{\circ}} \times 100\%$$

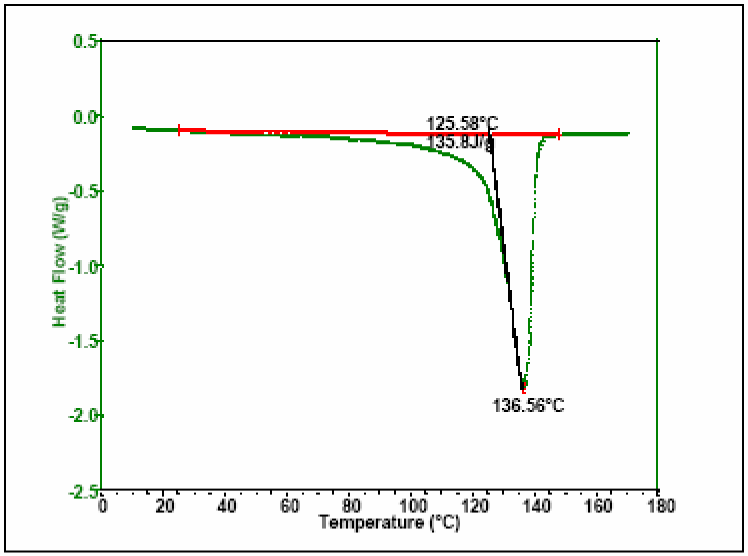


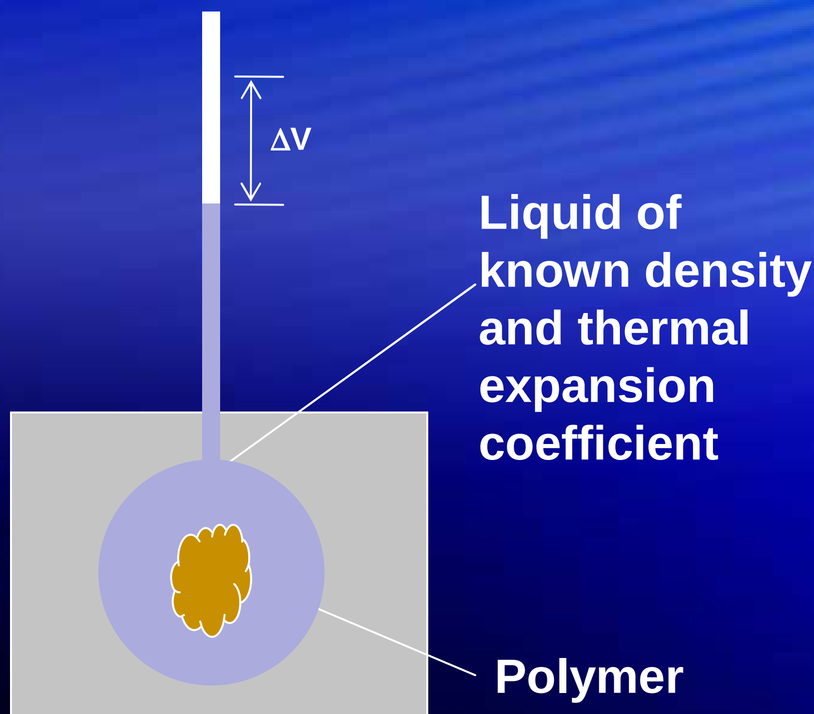

**Table: Heats of fusion of 100% crystalline polymers**

| Acronym (*4*) | Name | Enthalpy (kJ/mol) (*3*) | Repeat Unit | Molecular Weight (g/mol) | Enthalpy (J/g) |
|---|---|---|---|---|---|
| PE | Polyethylene | 4.11 | $-CH_2-$ | 14.03 | 293 |
| PP | Polypropylene | 8.70 | $-CH_2CH(CH_3)-$ | 42.08 | 207 |
| PB | Polybutene-1 | 7.00 | $-CH_2CH(C_2H_5)$ | 56.1 | 125 |
| POM | Polymethylenoxide | 9.79 | $-CH_2O-$ | 30.03 | 326 |
| PEOX | Polyethyleneoxide | 8.66 | $-CH_2CH_2O-$ | 44.05 | 197 |
| PA6 | Polycaprolactam | 26.0 | $-NH(CH_2)_5CO-$ | 113.2 | 230 |
| PA11 | Polyundecanolactam | 44.7 | $-NH(CH_2)_{10}CO-$ | 183.3 | 244 |
| PA12 | Polylauryllactam | 48.4 | $-NH(CH_2)_{11}CO-$ | 197.3 | 245 |
| PA66 | Poly(hexamethylene adipamide) | 57.8 | $-NH(CH_2)_6NHCO(CH_2)_4CO-$ | 256.3 | 226 |
| PA69 | Poly(hexamethylene nonanediamide) | 69 | $-NH(CH_2)_6NHCO(CH_2)_7CO-$ | 268.4 | 257 |
| PA610 | Poly(hexamethylene sebacamide) | 71.7 | $-NH(CH_2)_6NHCO(CH_2)_8CO-$ | 282.4 | 254 |
| PA612 | Poly(hexamethylene dodecanediamide) | 80.1 | $-NH(CH_2)_6NHCO(CH_2)_{10}CO-$ | 310.5 | 258 |
| PVOH | Polyvinyl alcohol | 7.11 | $-CH_2CH(OH)-$ | 44.05 | 161 |
| PET | Polyethylene terephathalate | 26.9 | $-O(CH_2)_2O_2CC_6H_4CO-$ | 192.2 | 140 |
| PBT | Polybutylene terephathalate | 32.0 | $-O(CH_2)_4O_2CC_6H_4CO-$ | 220.2 | 145 |
| PVF | Polyvinyl fluoride | 7.54 | $-CH_2CH(F)-$ | 46.04 | 164 |
| PVDF | Polyvinylidene fluoride | 6.70 | $-CH_2CF_2-$ | 64.03 | 105 |
| | Polytrifluoroethylene | 5.44 | $-CH(F)CF_2-$ | 82.0 | 66.3 |
| PTFE | Polytetrafluoroethylene | 4.10 | $-CF_2-$ | 50.0 | 82.0 |
| PVC | Polyvinyl chloride | 11.0 | $-CH_2CH(Cl)-$ | 62.50 | 176 |
| PCTFE | Polychlorotrifluoroethylene | 5.02 | $-CF_2CF(Cl)-$ | 116.5 | 43.1 |
| PEEK | Polyetheretherketone | 37.4 | $-C_6H_4COC_6H_4OC_6H_4O-$ | 288.3 | 130 |

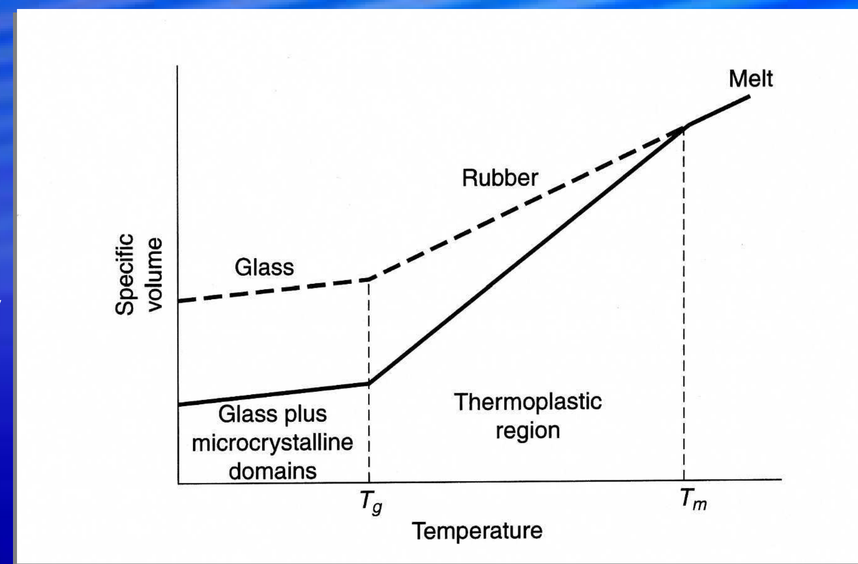
**Q: "Where is my polymer in this table?"**

# Dilatometry

## *Dilation* or change in specific volume

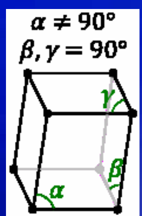


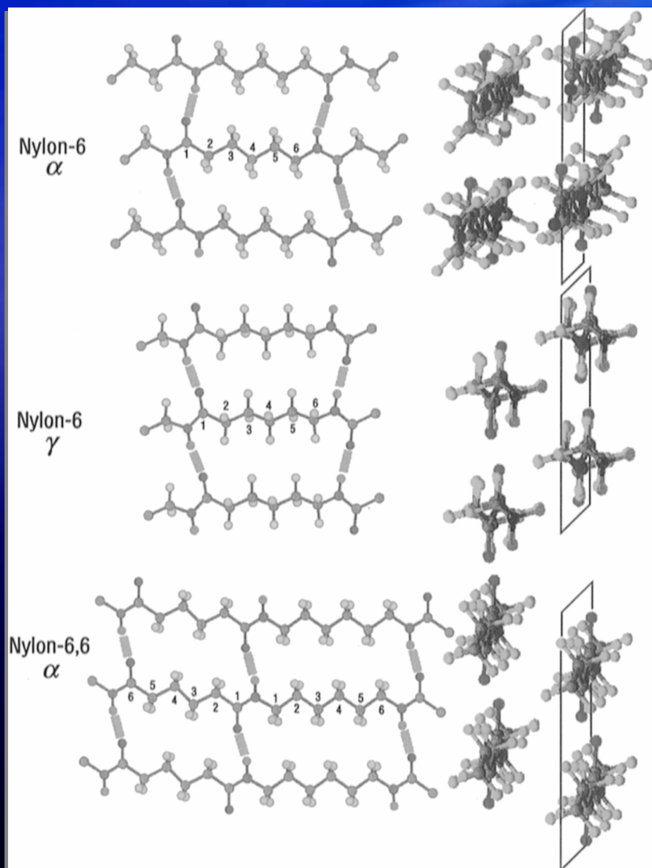

## Computing crystallinity




$$\%C = \frac{v_{amorphous} - v_{partially\ crystalline}}{v_{amorphous} - v_{totally\ crystalline}}$$

# Dilatometry



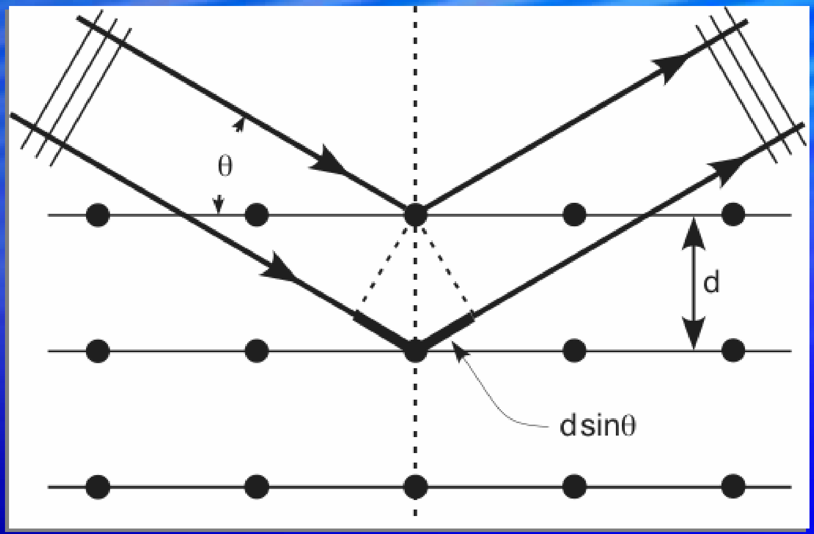

- Example: Nylon
- How would you find the density (i.e. specific volume) of this crystal given the size and shape?

$$\%C = \frac{v_{amorphous} - v_{partially\ crystalline}}{v_{amorphous} - v_{totally\ crystalline}}$$

Youyong Li and, William A. Goddard III
Macromolecules 2002 35 (22), 8440-8455

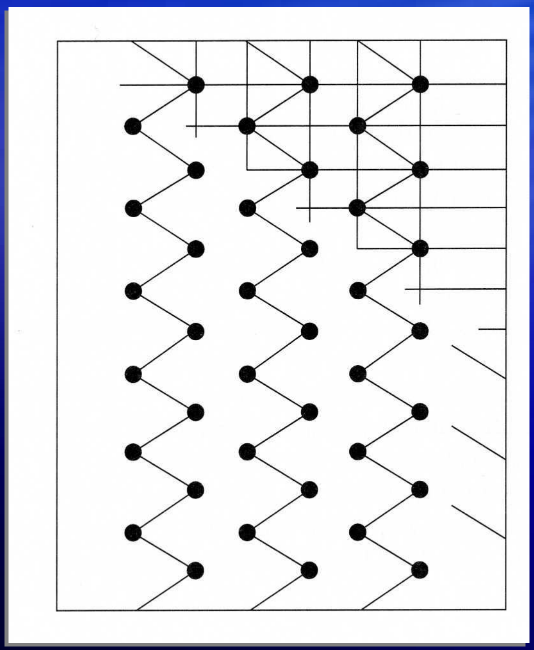
# Wide angle x-ray scattering/diffraction

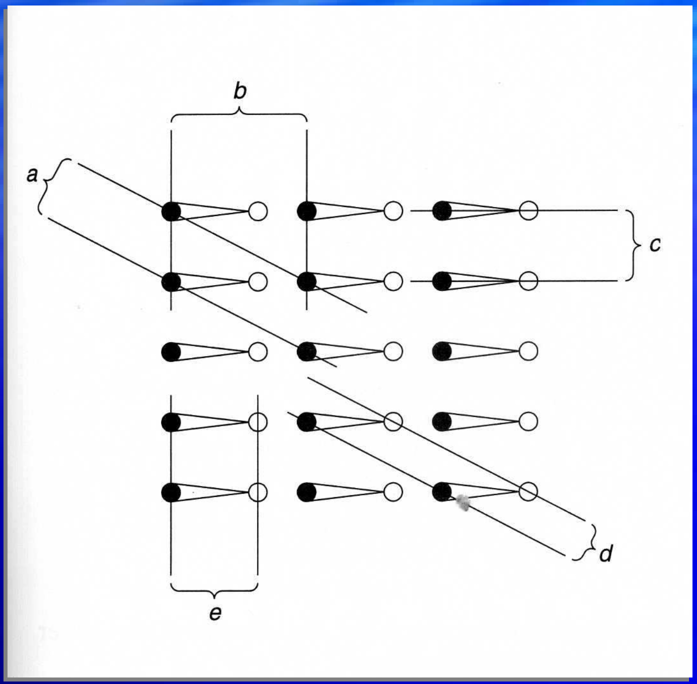
- X-rays: light with wavelength ~0.1-10Å – the same length scale as interatomic distances
- Diffraction occurs only at specific angles, given by the Bragg eqn.




$$n\lambda = 2d\sin\theta$$

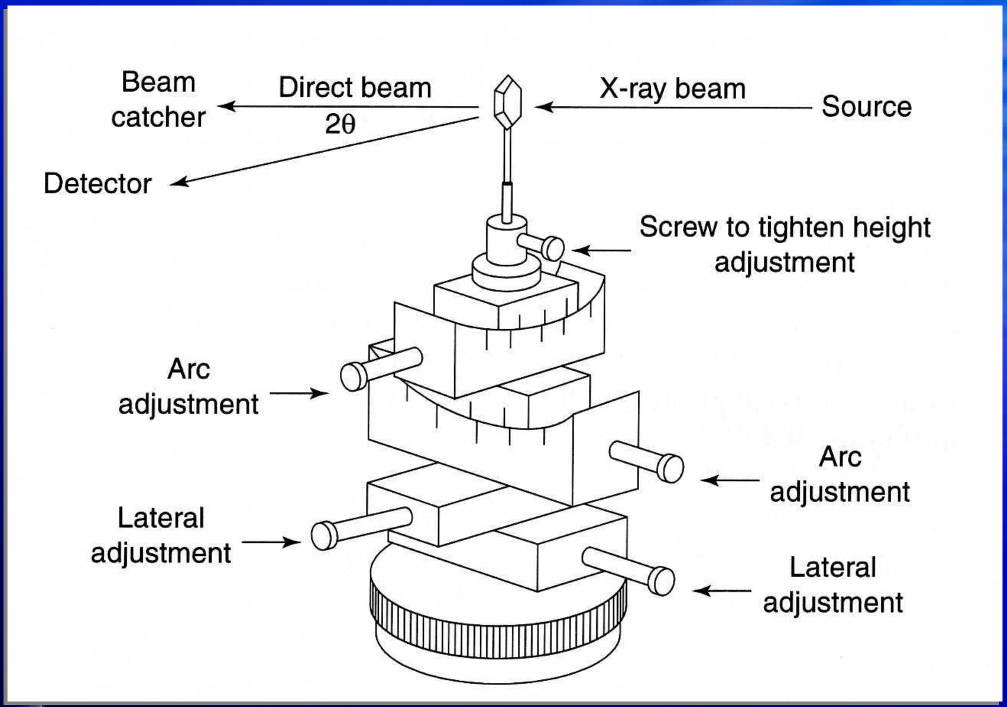
# X-ray Scattering Crystal Planes

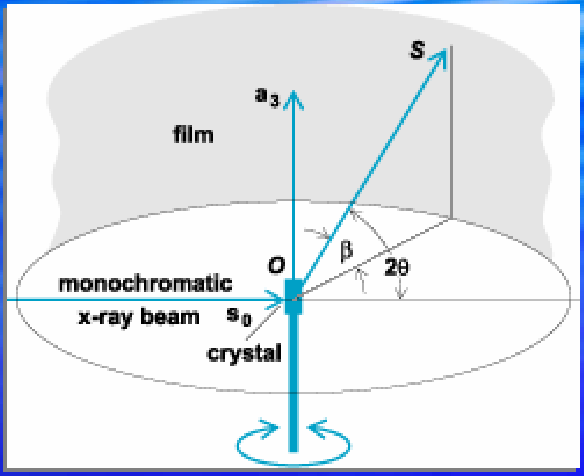


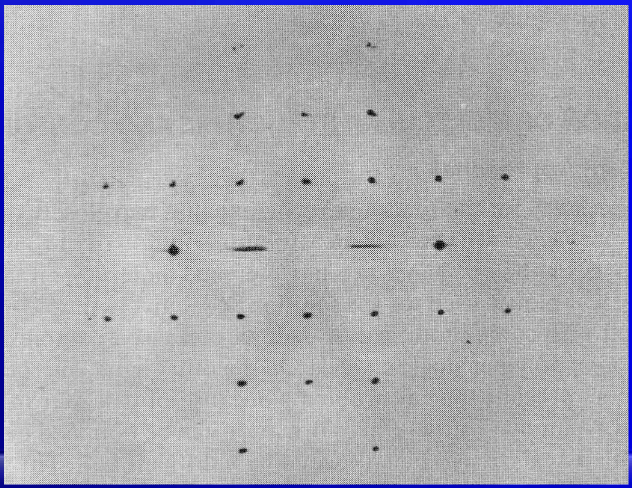



$$n\lambda = 2d\sin\theta$$

# Wide angle x-ray scattering/diffraction



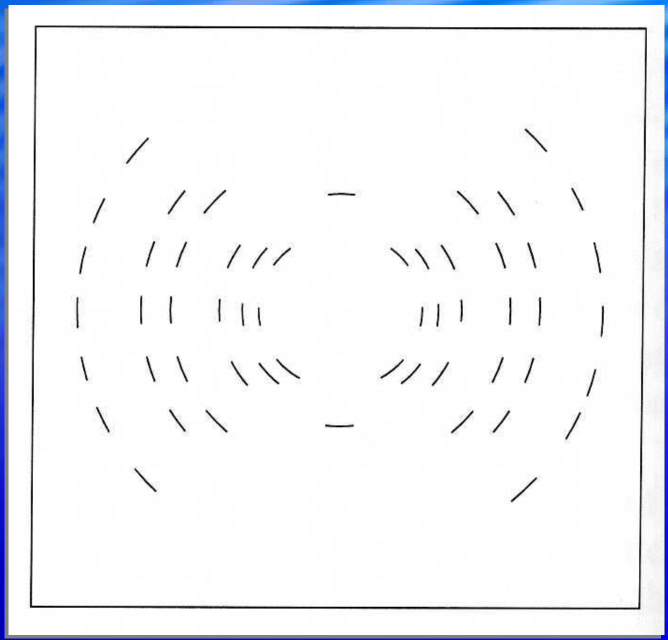



Why 2θ?

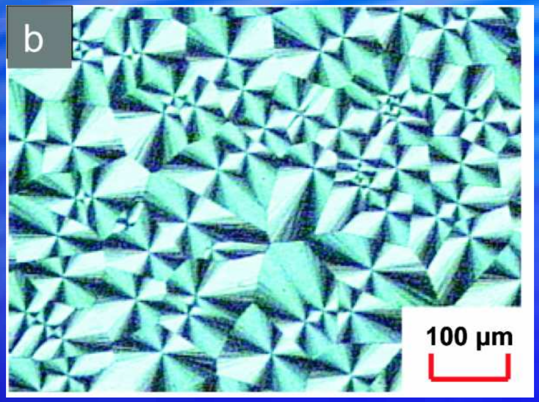
# What if it's not a single crystal?

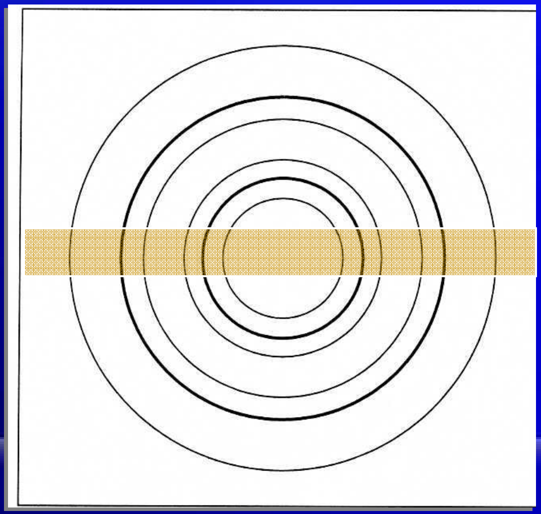
- Polycrystalline samples look different.
- Example: Highly crystalline polymer with (mostly) oriented crystallites.
- Diffraction spots are blurred into lines.



# What if it's not a single crystal?

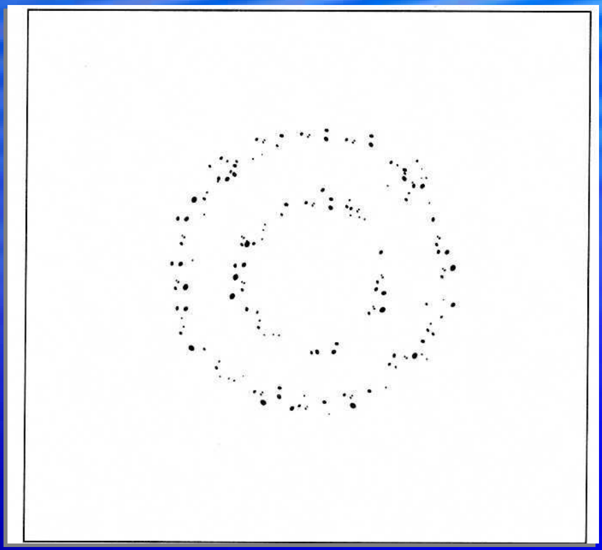
- Polycrystalline samples look different.
- Example: Highly crystalline polymer with no orientation of crystallites.
- Diffraction spots are blurred into full circles.



# What if it's not crystalline?

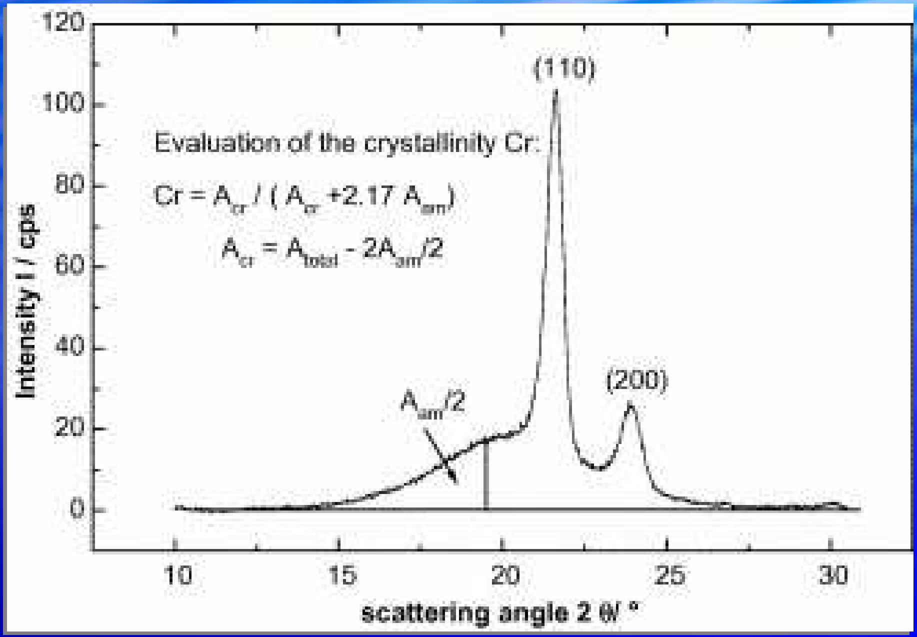
- Diffraction circles become much less defined and blurred.
- Sharpness of circles gives a clue to crystallinity.



# An estimate of crystallinity

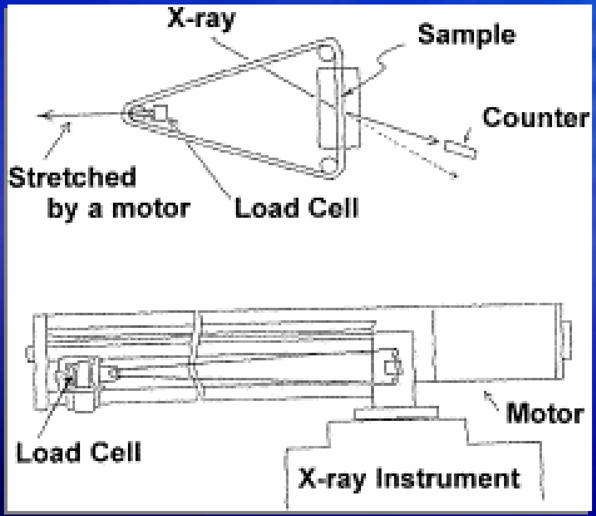
- The crystallinity can be estimated by comparing the areas of the peaks due to the amorphous polymer with those of the crystalline phase:

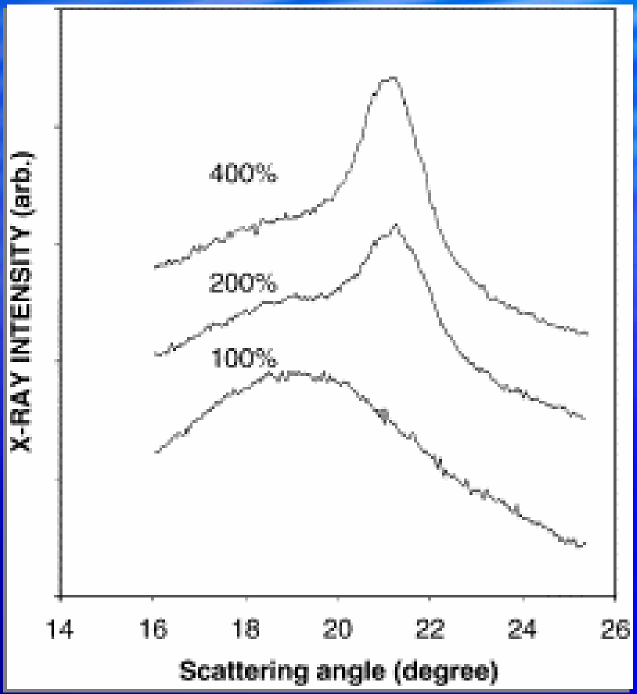
$$\%C = A_{cr} / (A_{cr} + A_{am})$$




K.A. Moly et al. / European Polymer Journal 41 (2005) 1410–1419;

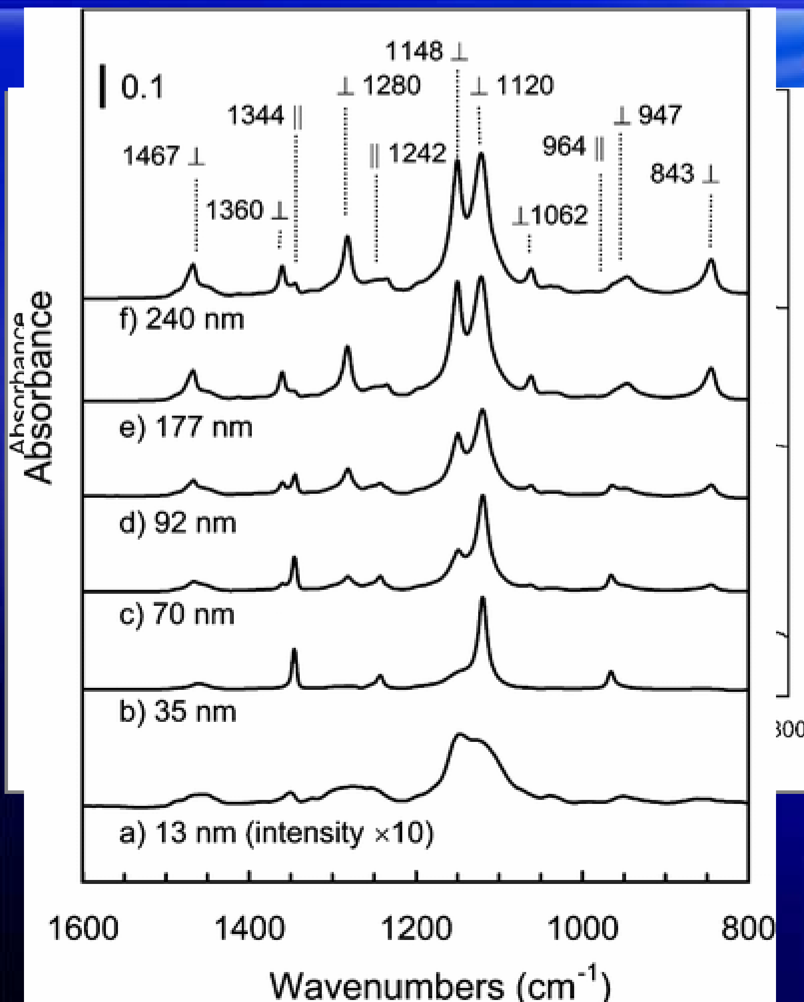
# Example: Strain-induced Crystallization

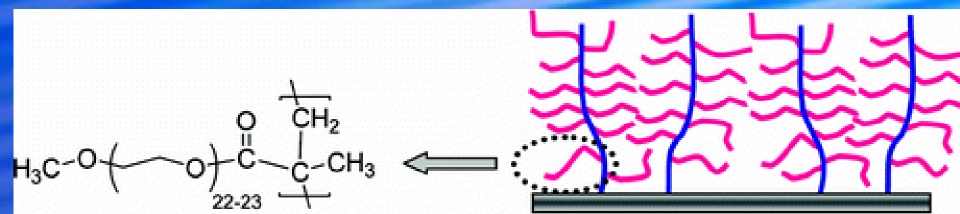


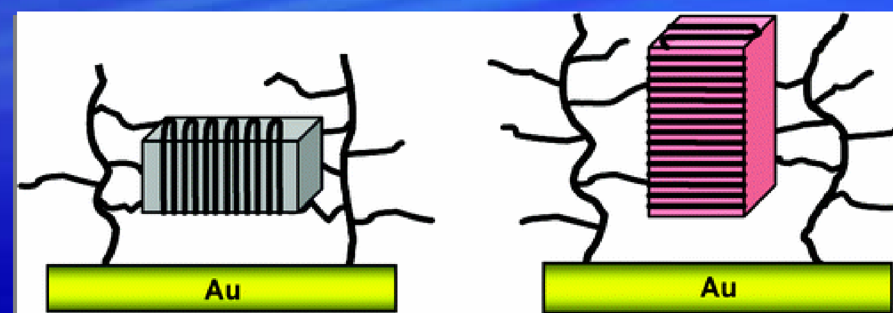




*S. Toki et al. / Polymer 41 (2000) 5423–5429*

# Other methods: IR & NMR




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

# Conclusion: A comparison

| Method of Analysis | Advantages | Disadvantages |
|---|---|---|
| Differential Scanning Calorimetry | Fast, easy; You're probably going to use DSC anyway for $T_g$, etc. | Need literature values of heat of fusion for 100% crystalline polymer for comparison; thermal history an issue. |
| Dilatometry | A simple way to measure polymer crystallinity based on changes in volume. | Pure crystalline specific volume must be known. |
| X-ray scattering | Can determine precise crystal structure. | Difficult to analyze data, determine structure. |
| Polarized Optical Microscopy | A quick way to see if a polymer is crystalline. | Other factors (like strain in the polymer) can cause birefringence; difficult to quantify. |

# 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?