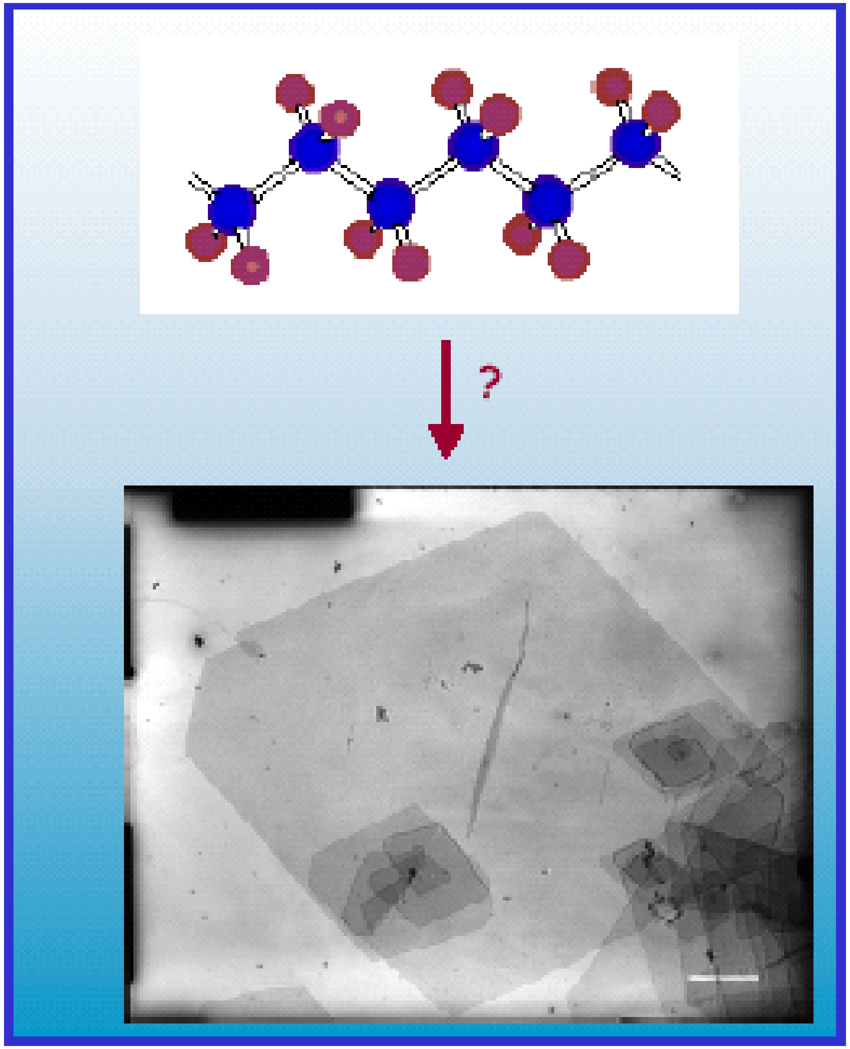
Structure and Morphology

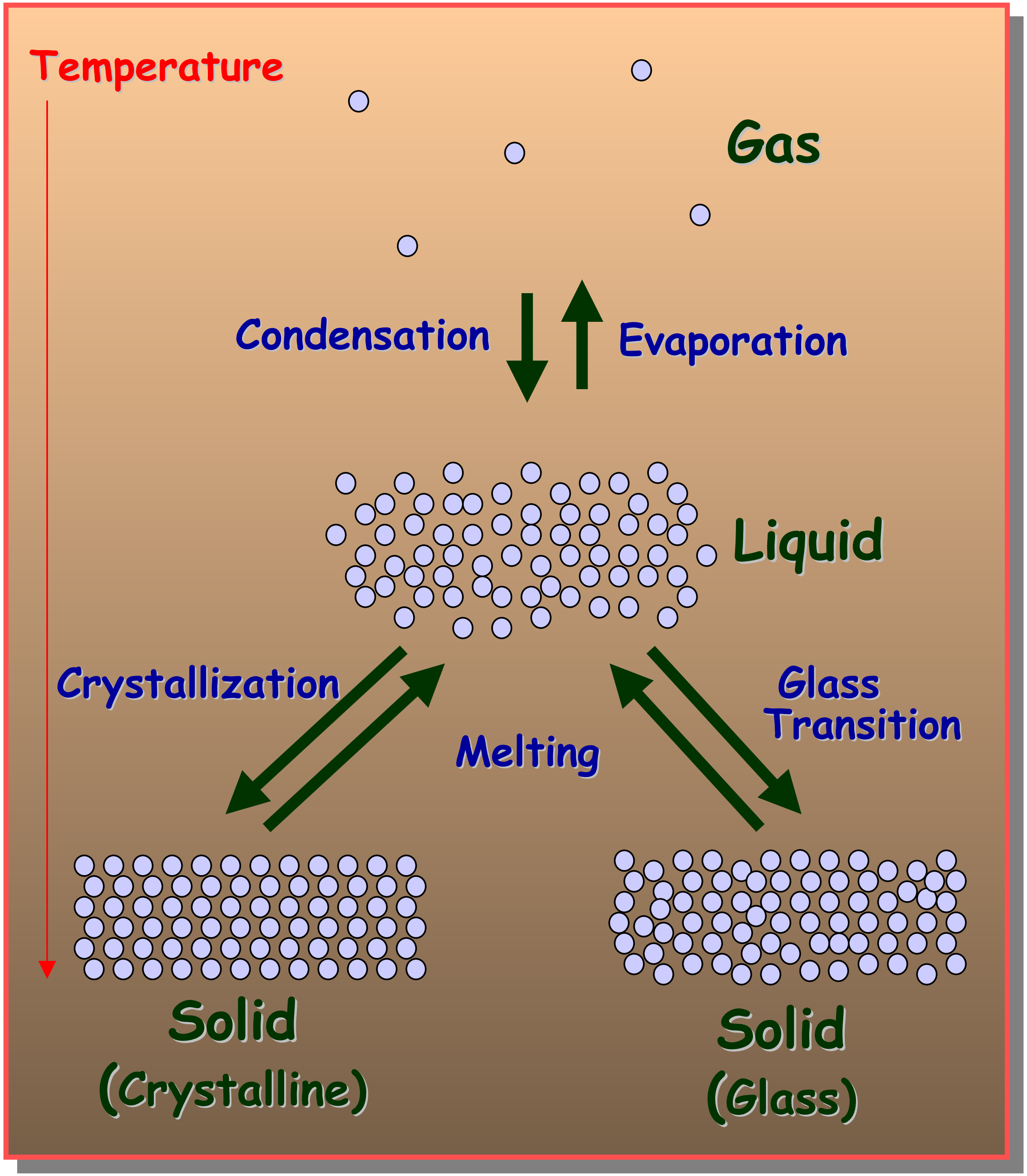
- Into what types of overall shapes or conformations can polymer chains arrange themselves?
- How do polymer chains interact with one another.
- Into what types of forms or morphologies do the chains organize
- What is the relationship of conformation and morphology to polymer microstructure.
- What is the relationship of conformation and morphology to macroscopic properties.



States of Matter

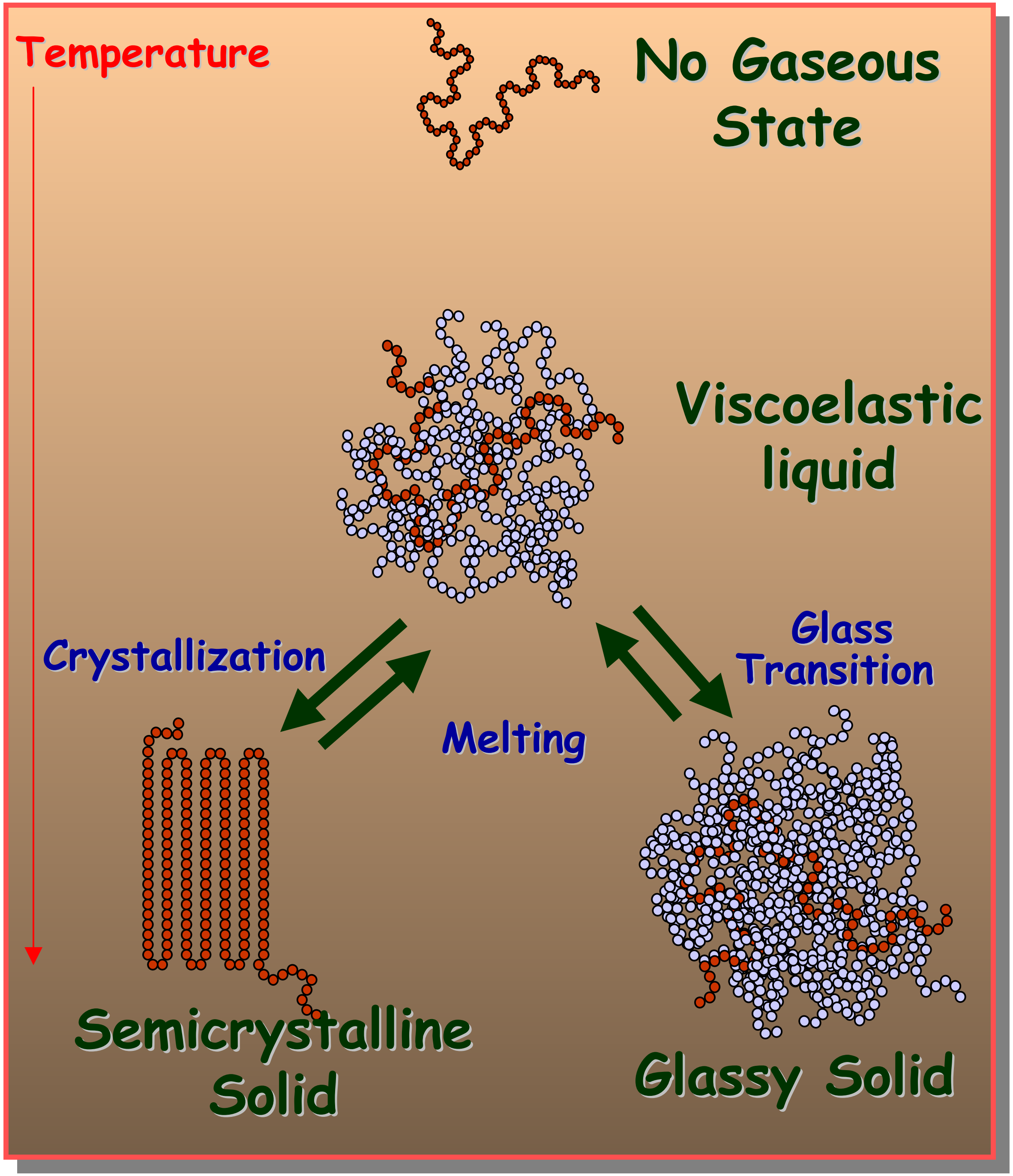
Usually consider;

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



Polymers

More complex behaviour



States of Matter

Small Molecules → Gas

"1st-Order" Transitions → Liquid, Solid

Gas

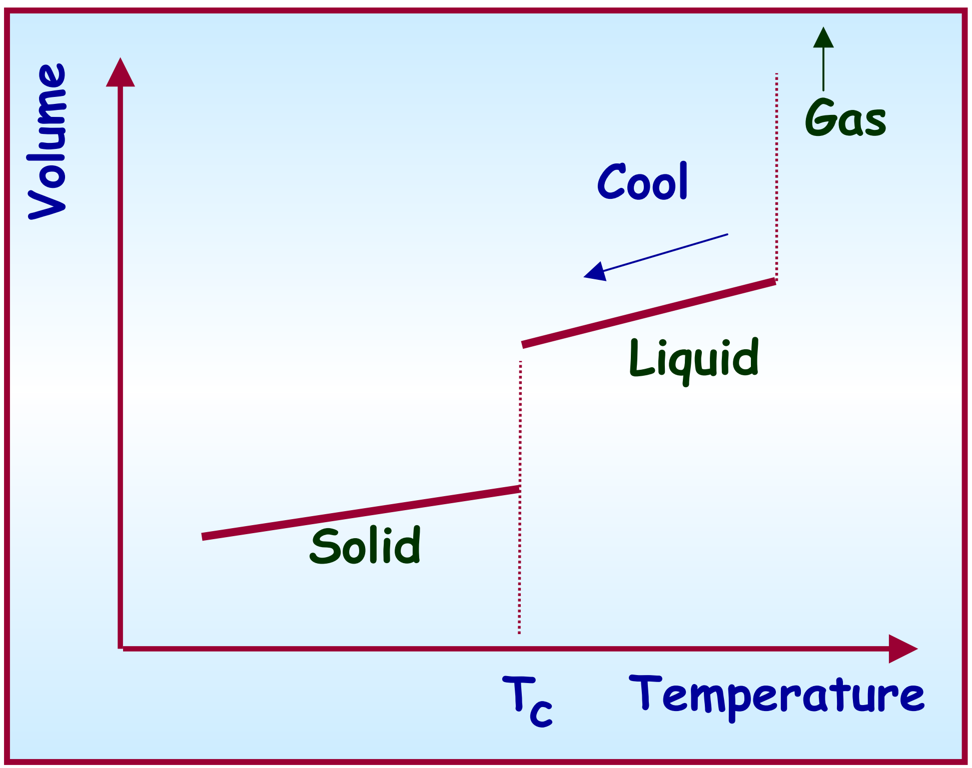
↓

Liquid

↓

Solid

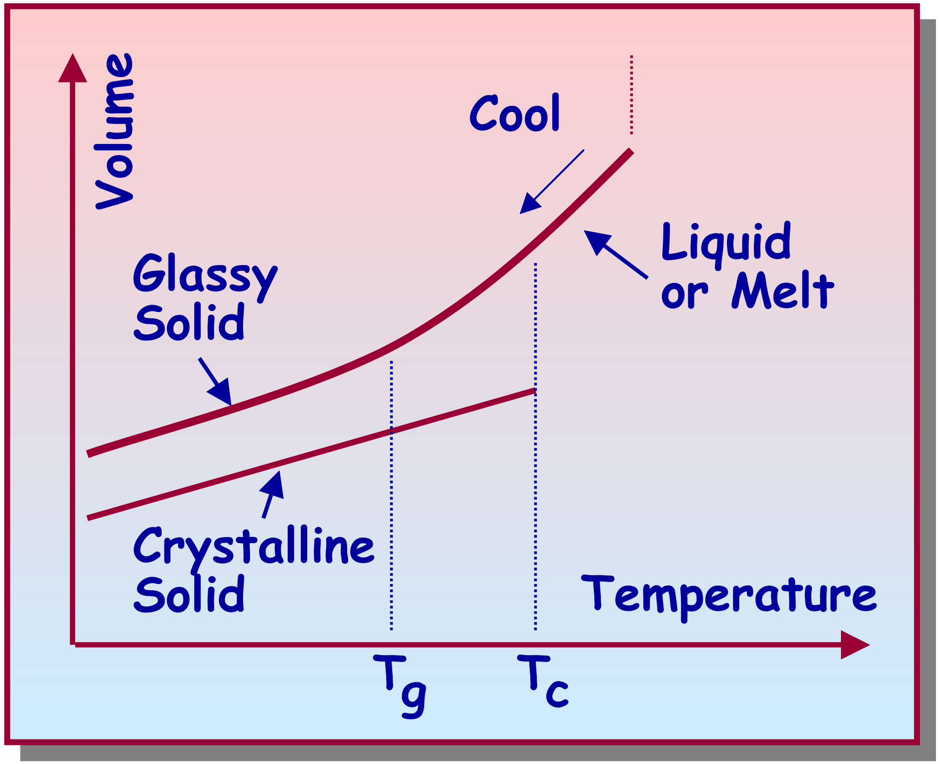
(Crystalline)



The Glassy State

Observed Behavior depends on:

- *Structure*
- *Cooling Rate*
- *Crystallization Kinetics*



Crystallizable materials can form metastable glasses.

What about polymers like atactic polystyrene that cannot crystallize?

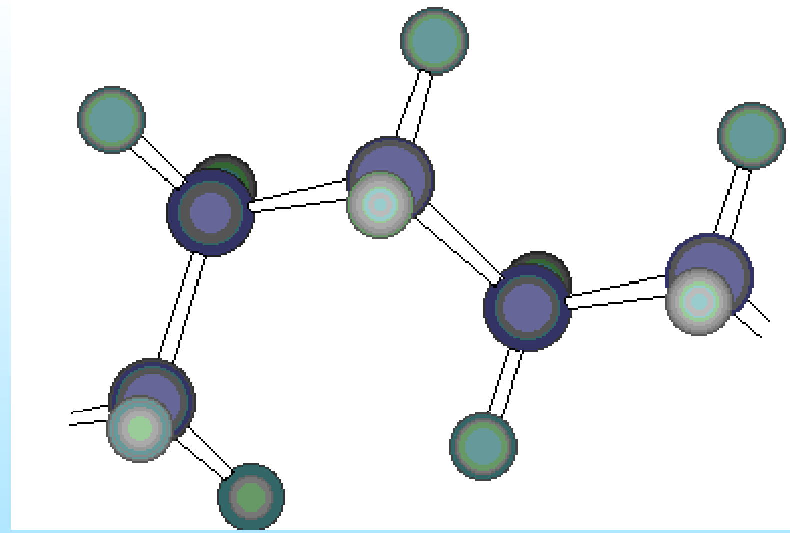
Polymer Structure

The Issues

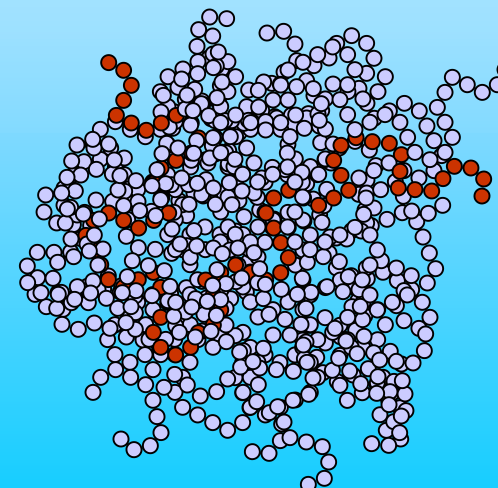
- *Bonding & the Forces between Chains*
- *Conformations*
  - *Ordered*
  - *Disordered*
- *Stacking or Arrangement of Chains in Crystalline Domains*
- *Morphology of Polymer Crystals*

Bonding and Intermolecular Interactions

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



What determines how close these chains pack?



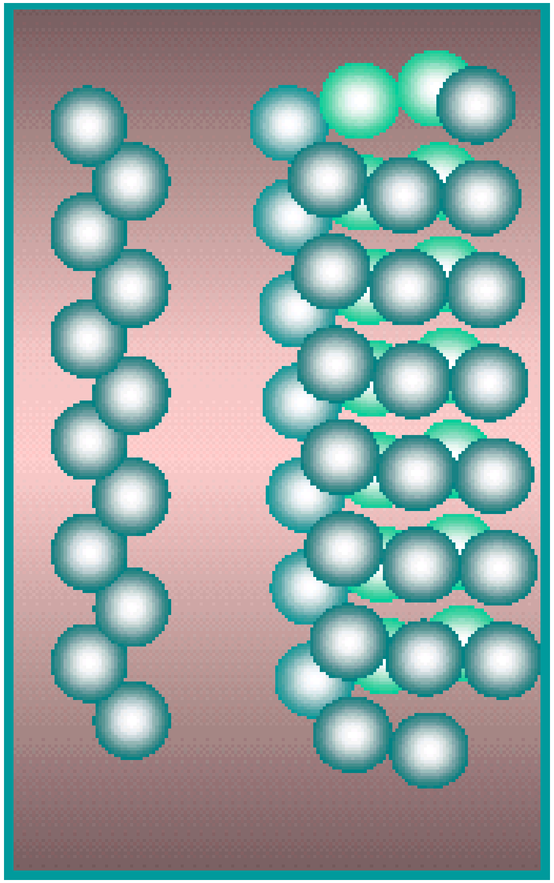
SUMMARY

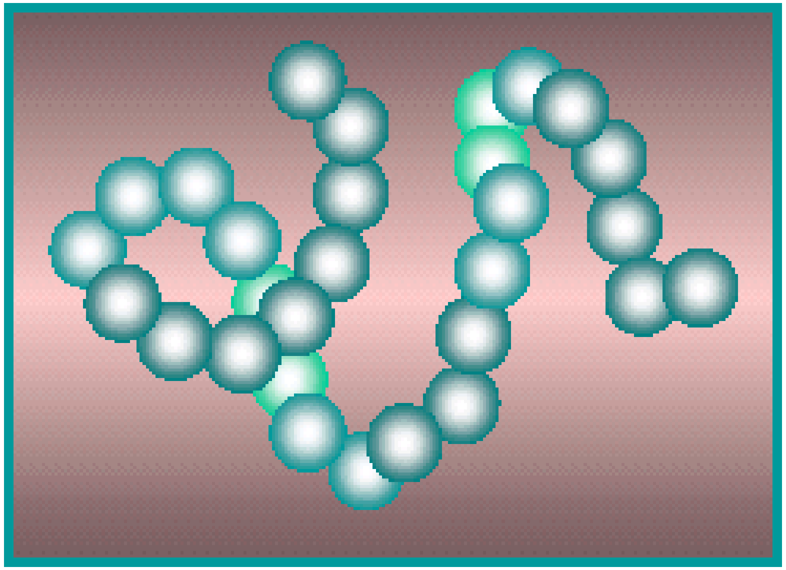
Type of Interaction	Characteristics	Approximate Strength	Examples
Dispersion Forces	Short Range Varies as $-1/r^6$	About 0.2 - 0.5 kcal/mole	Poly(ethylene) Polystyrene (simple hydrocarbon polymers)
Dipole/dipole Interactions (Freely Rotating)	Short Range Varies as $-1/r^6$	About 0.5 - 2 kcal/mole	Poly(acrylonitrile) PVC
Strong Polar Interactions and Hydrogen Bonds	Complex Form but also Short Range	About 1 - 10 kcal/mole	Nylons Poly(urethanes)
Coulombic Interactions (Ionomers)	Long Range Varies as $1/r$	About 10 - 20 kcal/mole	Surlyn

Increasing Interaction Strength

Conformations

Ordered





Disordered

Morphology

THE STUDY OF FORM AND STRUCTURE

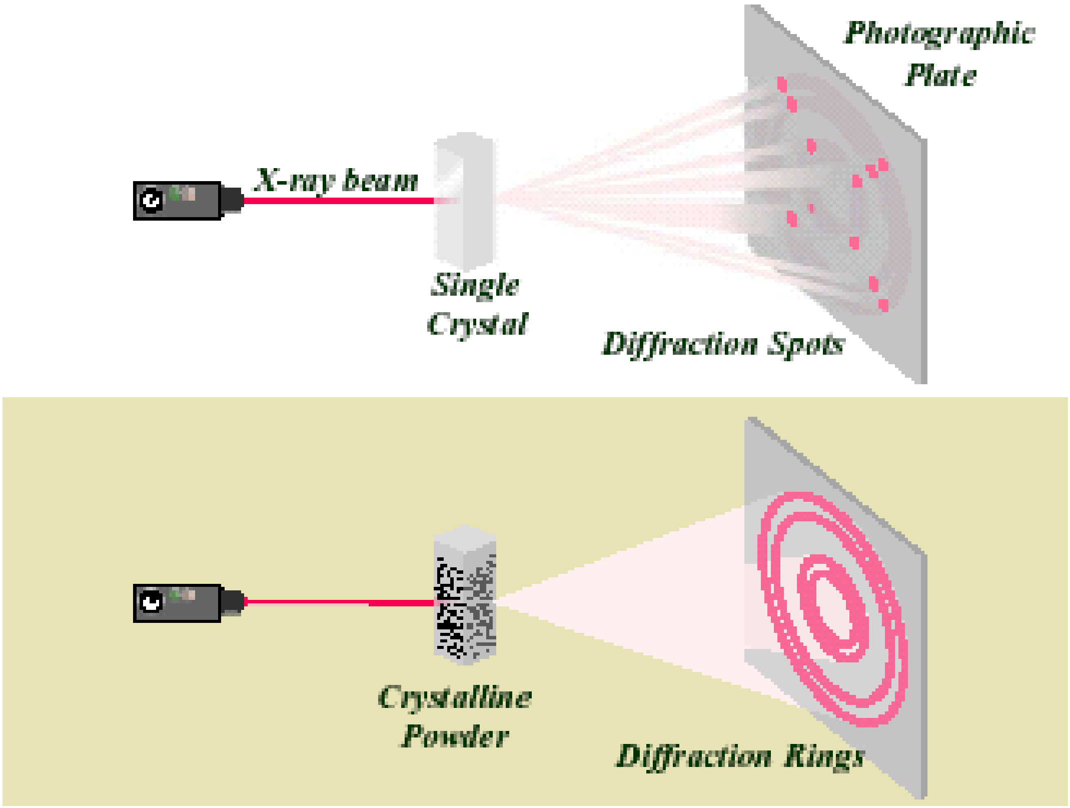
Polymer morphology - *the study of order within macromolecular solids*

Our focus;

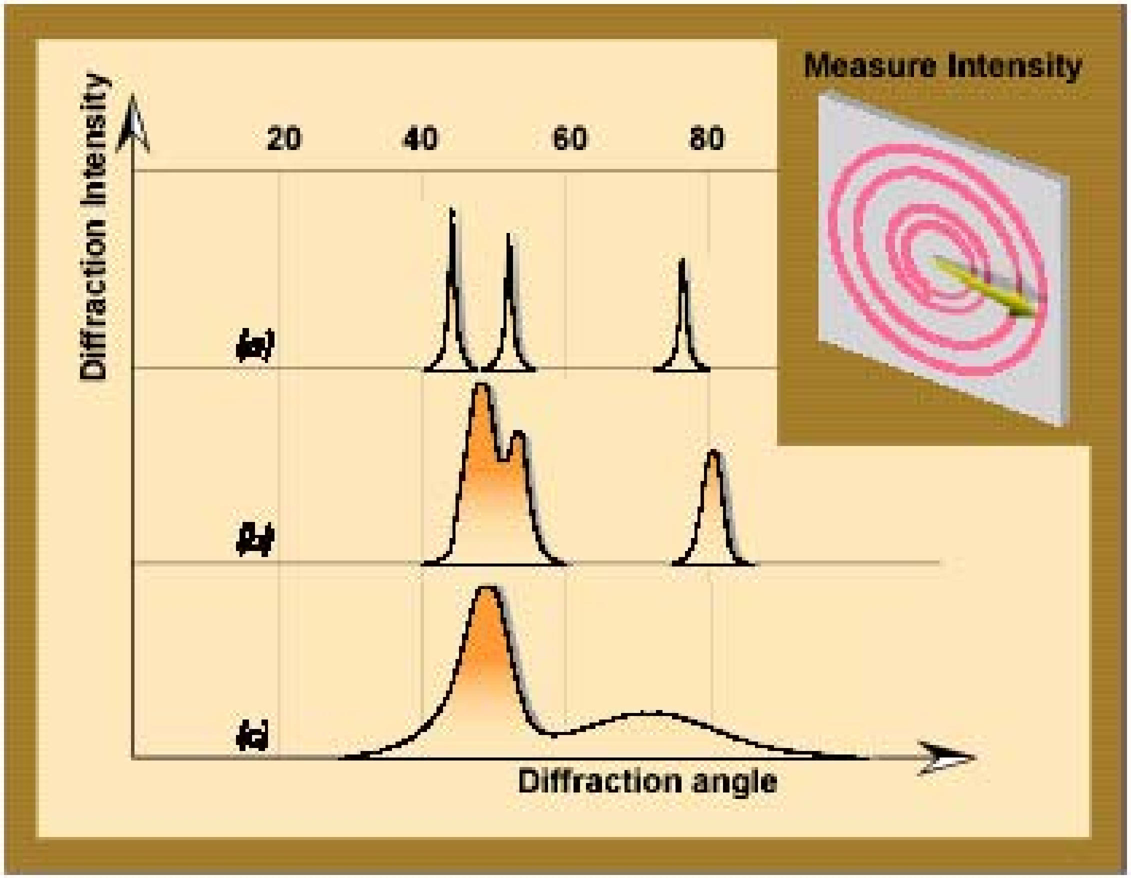
Morphology of semi - crystalline Polymers

Single crystal lamellae
Spherulites
Fibers

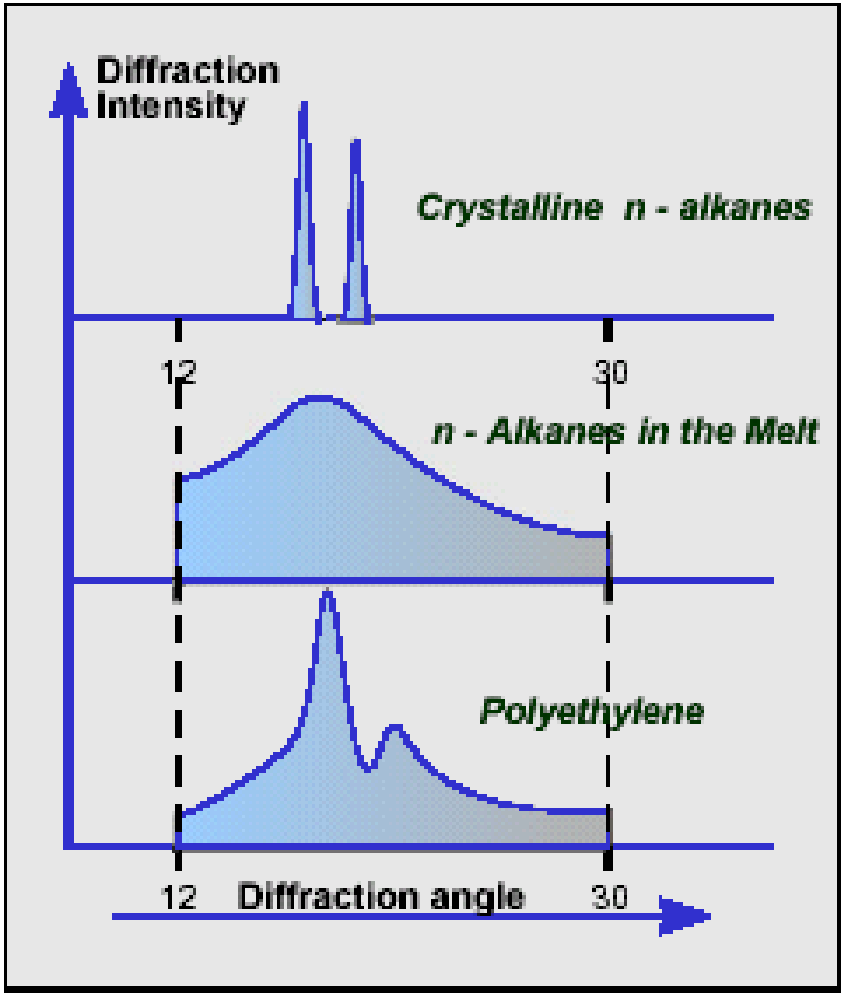
X-ray Diffraction



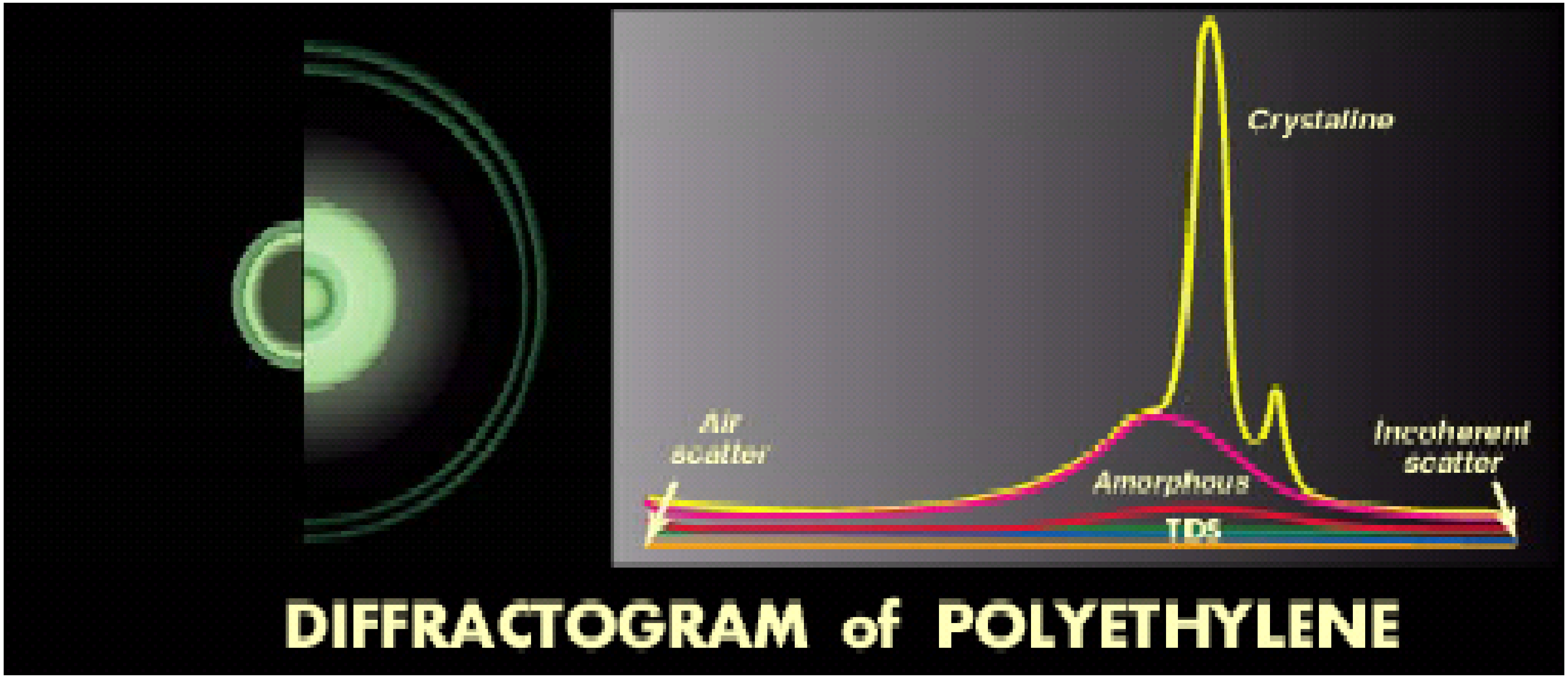
X-ray Diffraction



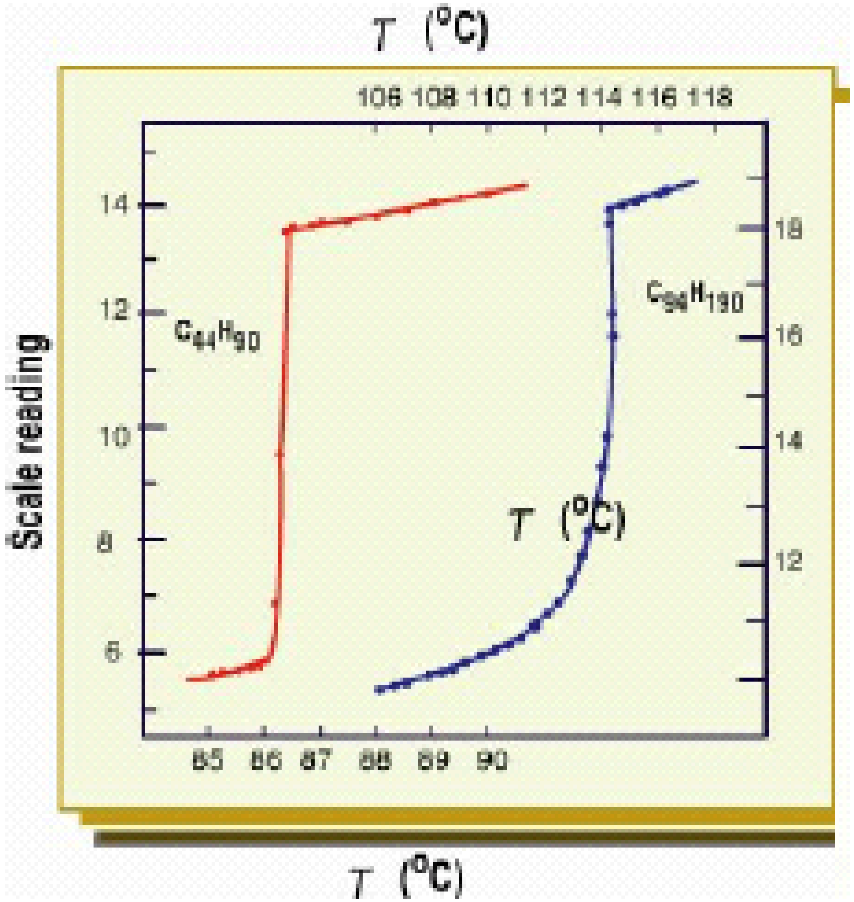
X-ray Diffraction; The n- Alkanes and Polyethylene

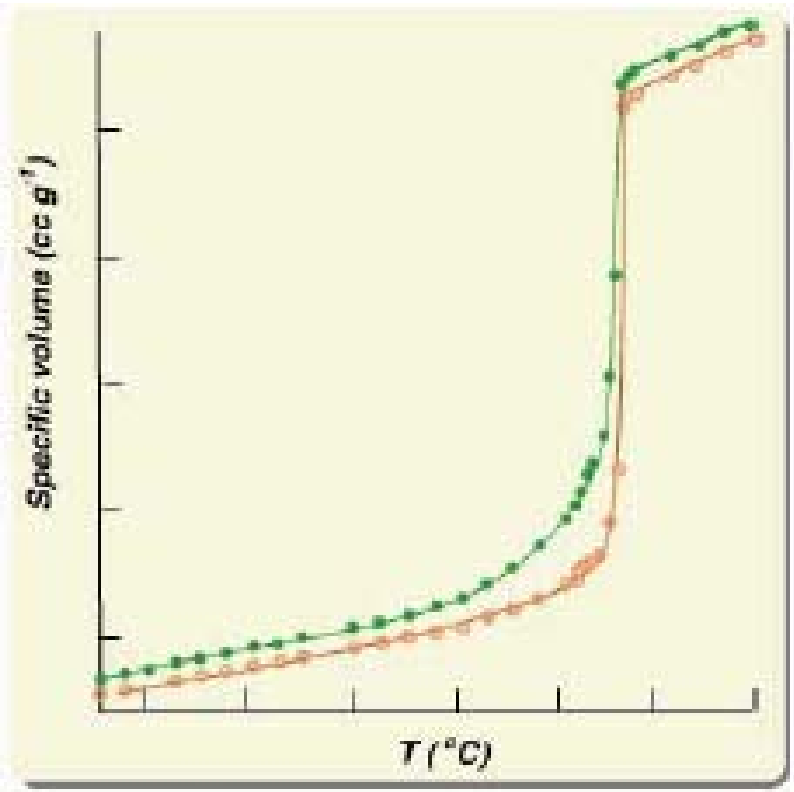


Polymers are Semicrystalline



Melting Temperatures





Crystallinity in Polymers

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

- CRYSTALLIZABLE POLYMERS
  - *Never 100% Crystalline*
  - *Melt over a Range of Temperatures*

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

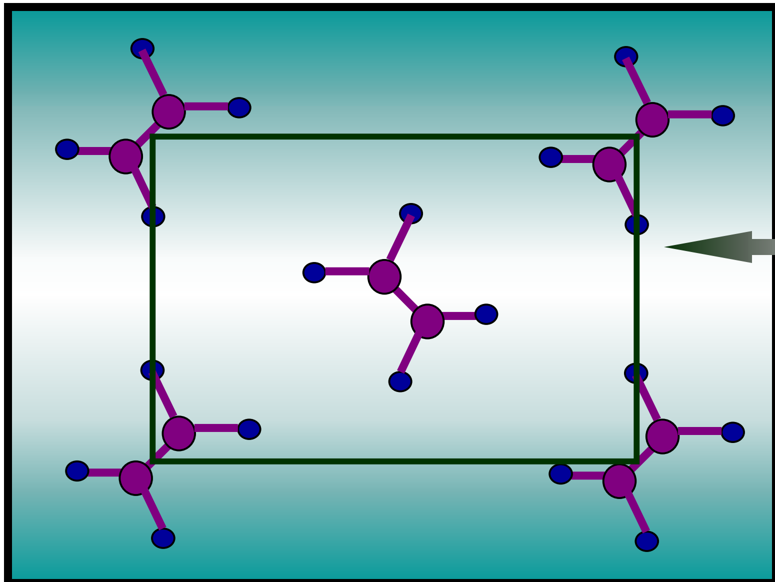
J.D.Hoffman,G.T.Davis,J.I.Lauritzen
In "Treatise on Solid State Chemistry"
N.B.Hannay,ed Vol 3, Ch7,Plenum Press
New York,1976

Questions

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

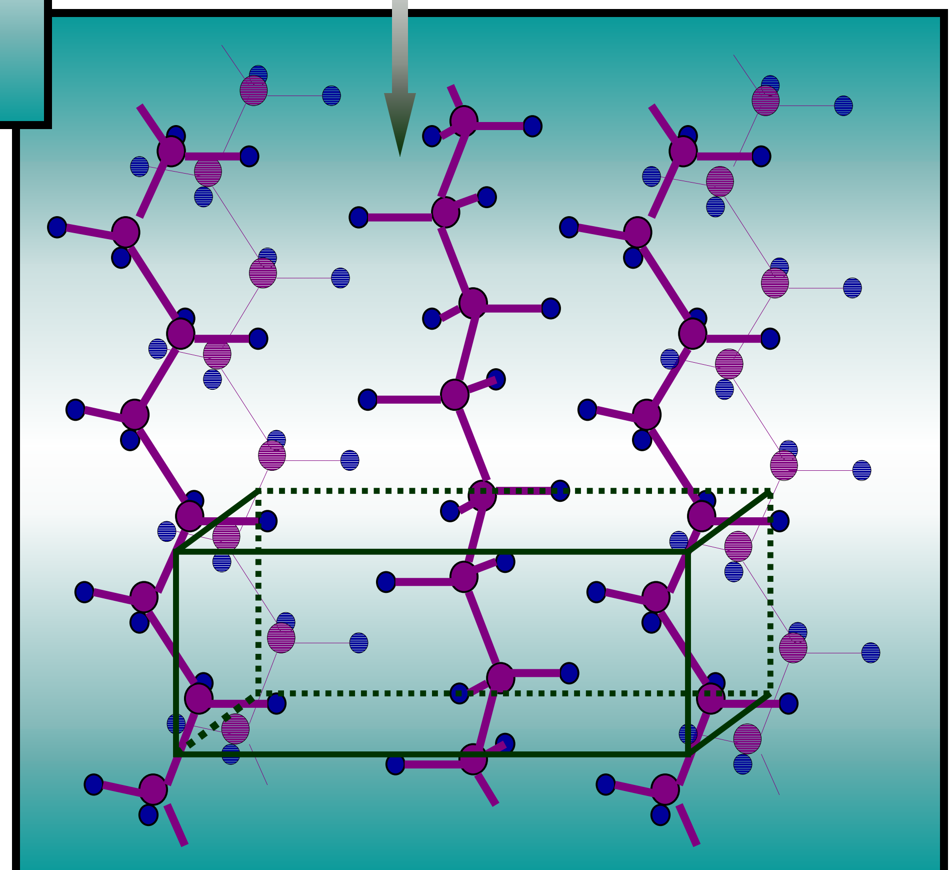
- ***What is the Conformation of the Chains in the Crystalline Domains and how are they Stacked relative to one another?***
- ***What is the Overall Shape and Form of the Crystals?***
- ***What are the Relative Arrangements of the Crystalline and Amorphous Parts?***

Polyethylene



Top view of Unit Cell

Side view



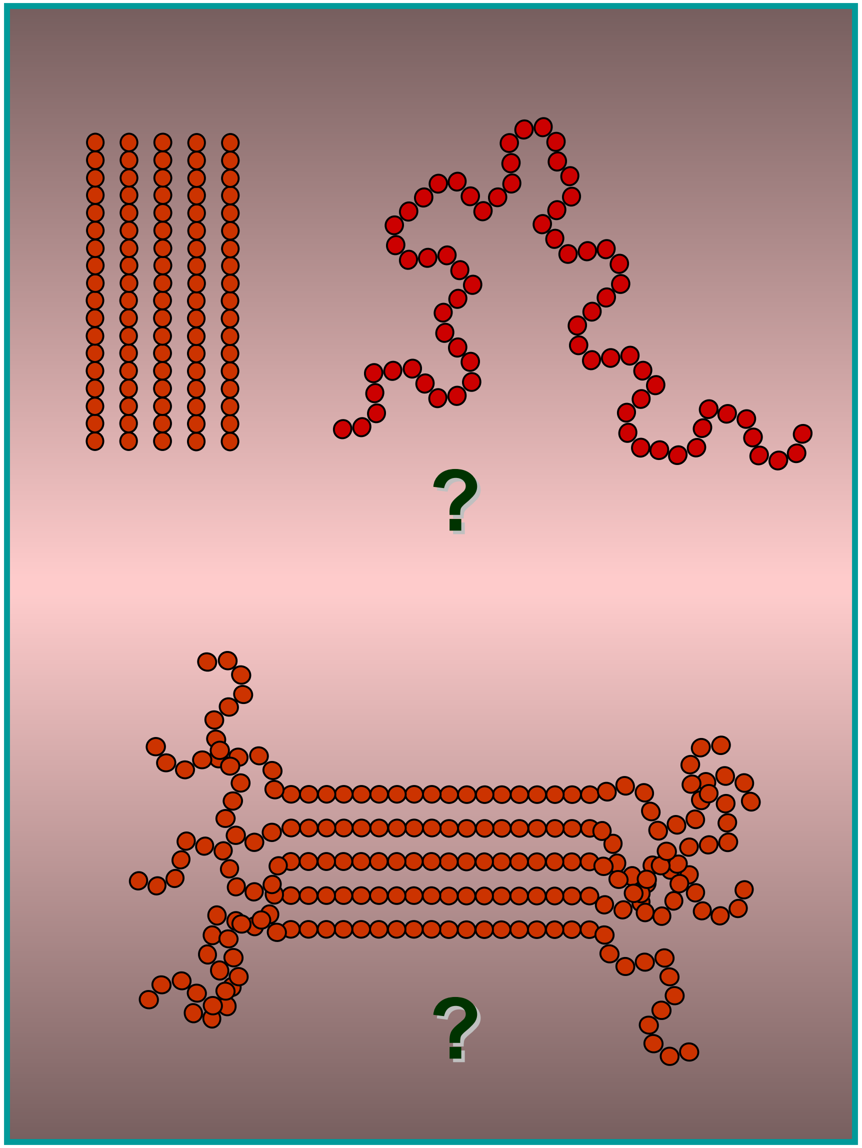
Redrawn from C. W. Bunn, Fibers from Synthetic Polymers, *R. Hill, Ed.,*
Elsevier Publishing Co., Amsterdam, 1953.

The unit cell contains segments of different chains.

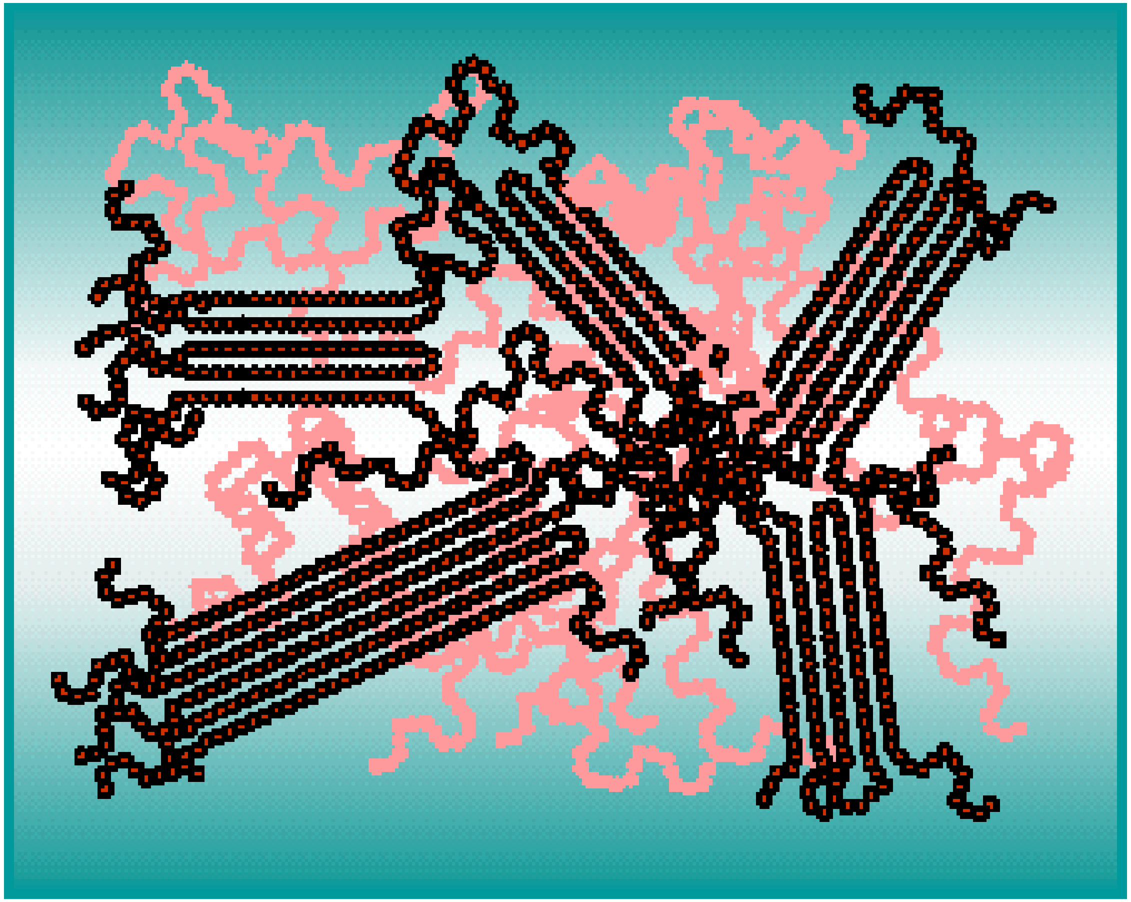
Chain Arrangements and Morphology

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

Do chains pass through both regions ?

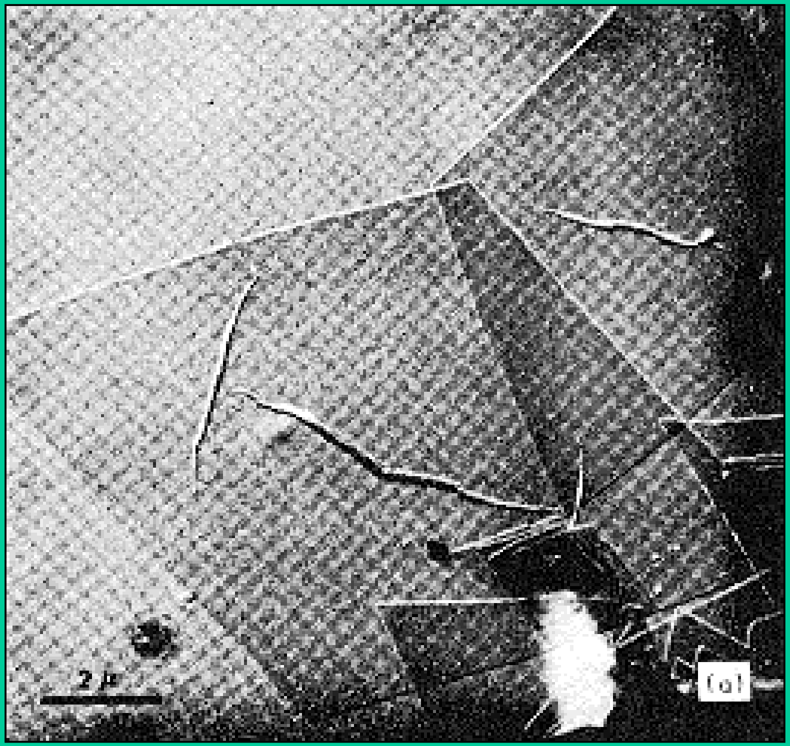


The Fringed Micelle Model

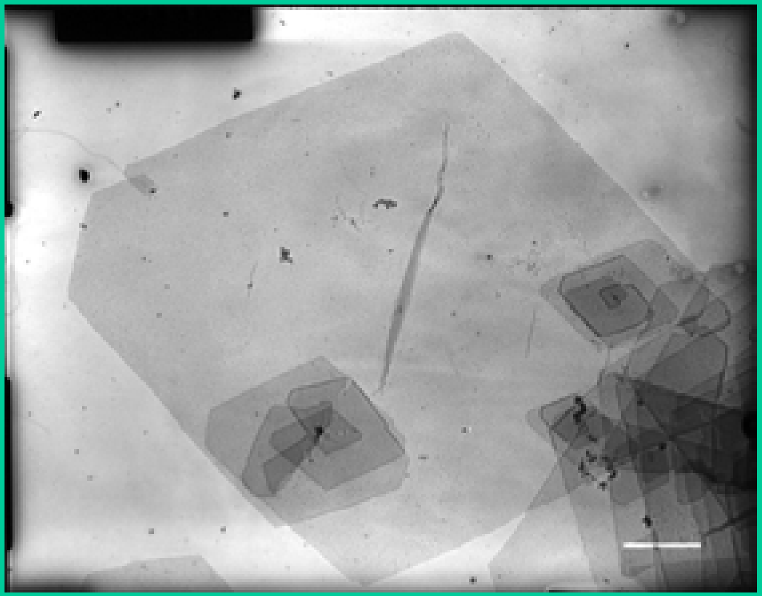


The First Really Useful Model

Single Crystal Lamellae

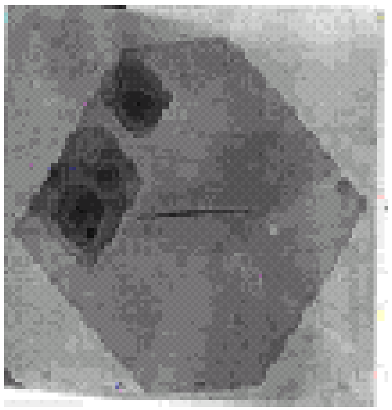


Reproduced with permission from P. H. Geil, *Polymer Single Crystals*, Robert E. Krieger Publishing Company, Huntington, New York, 1973.

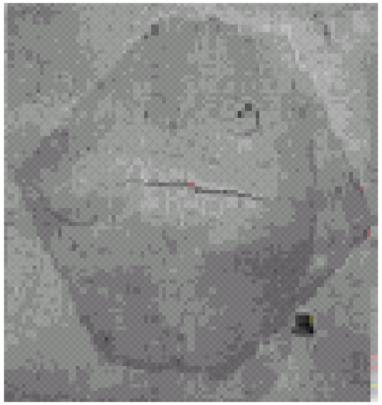


Courtesy of I.R. Harrison, Penn State

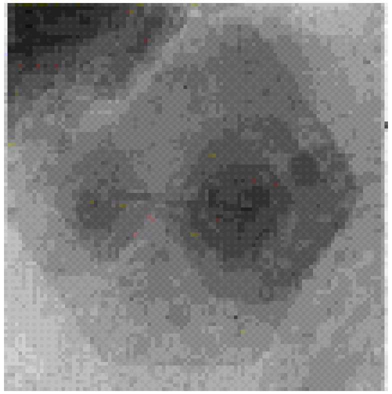
Polyethylene Single Crystals



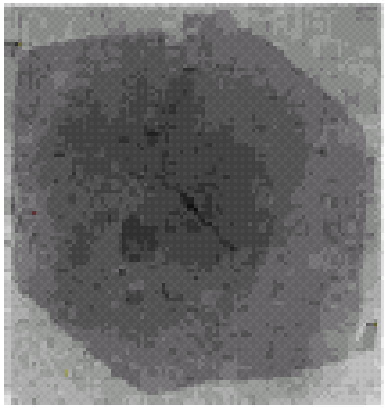
85^{0}C



87^{0}C



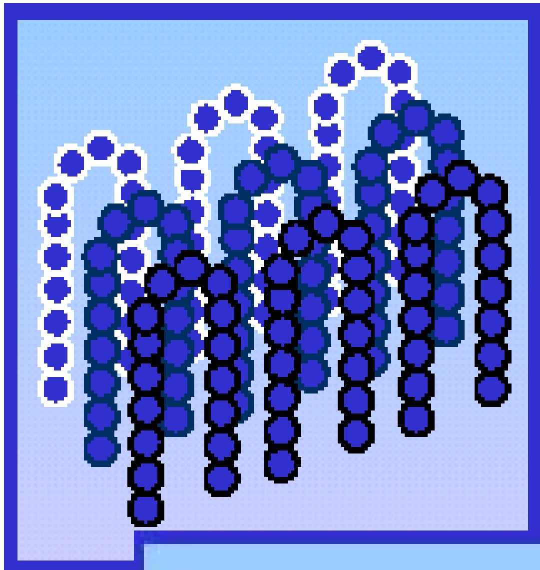
90^{0}C

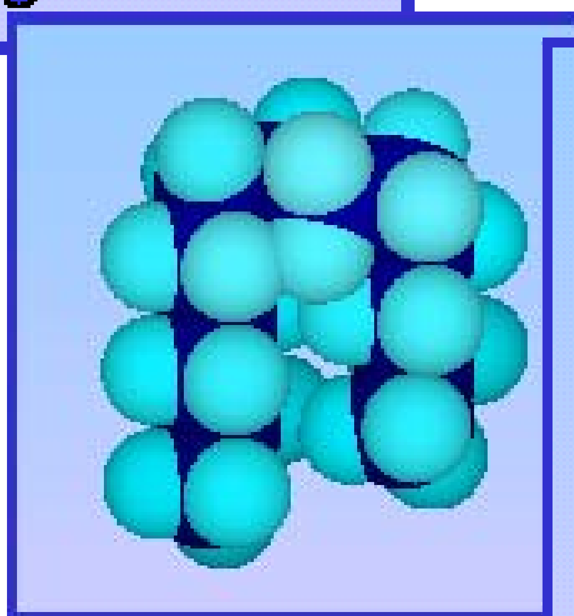


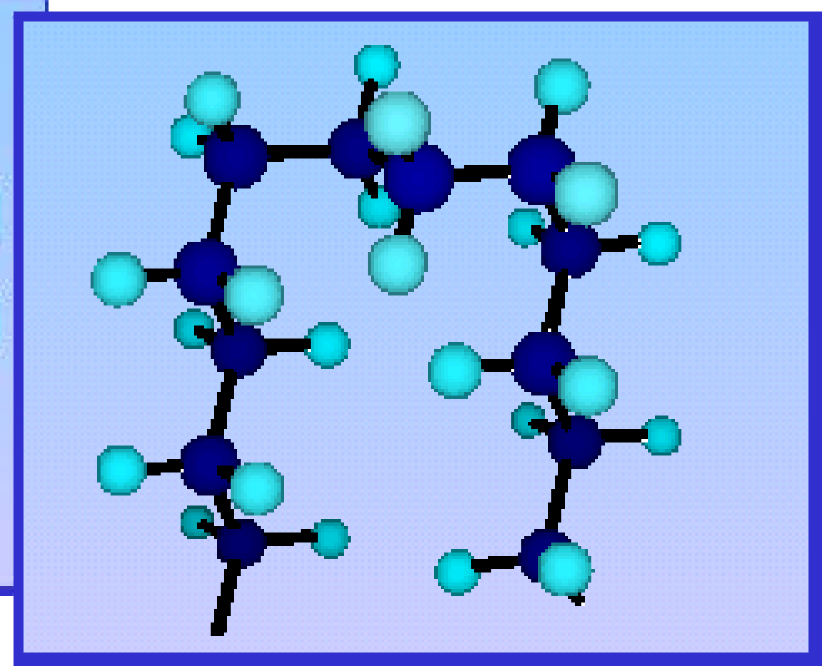
93^{0}C

95^{0}C

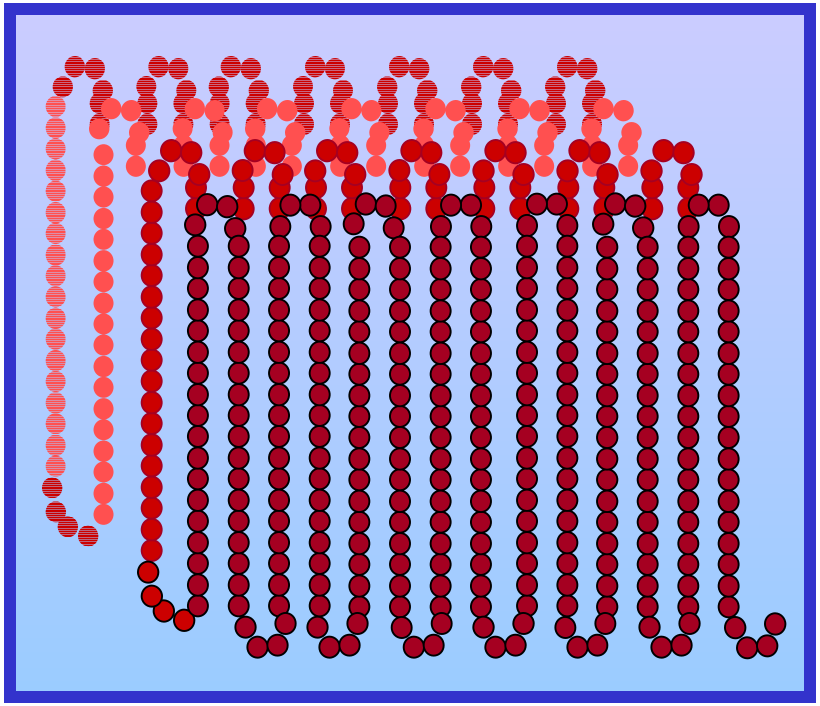
Regular Chain Folding



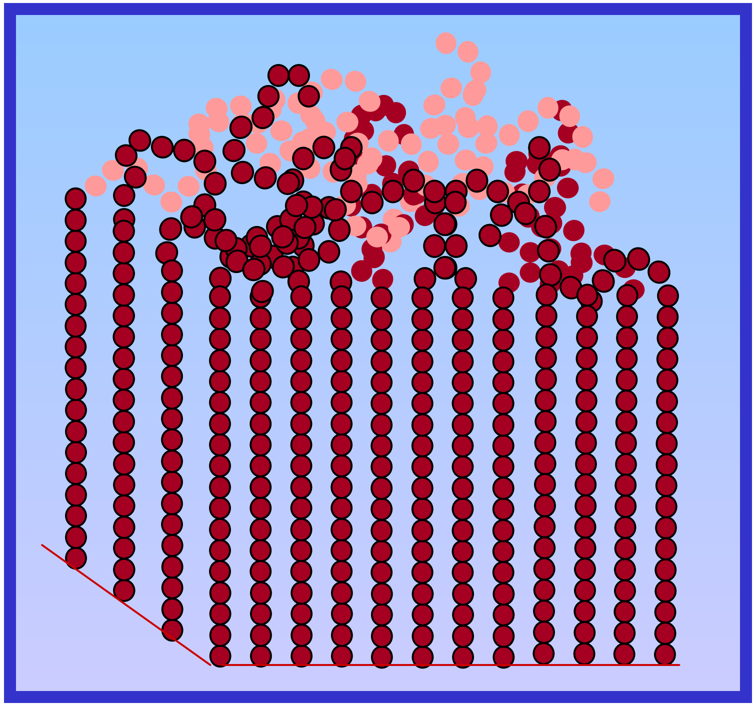




The Flory Switchboard Model

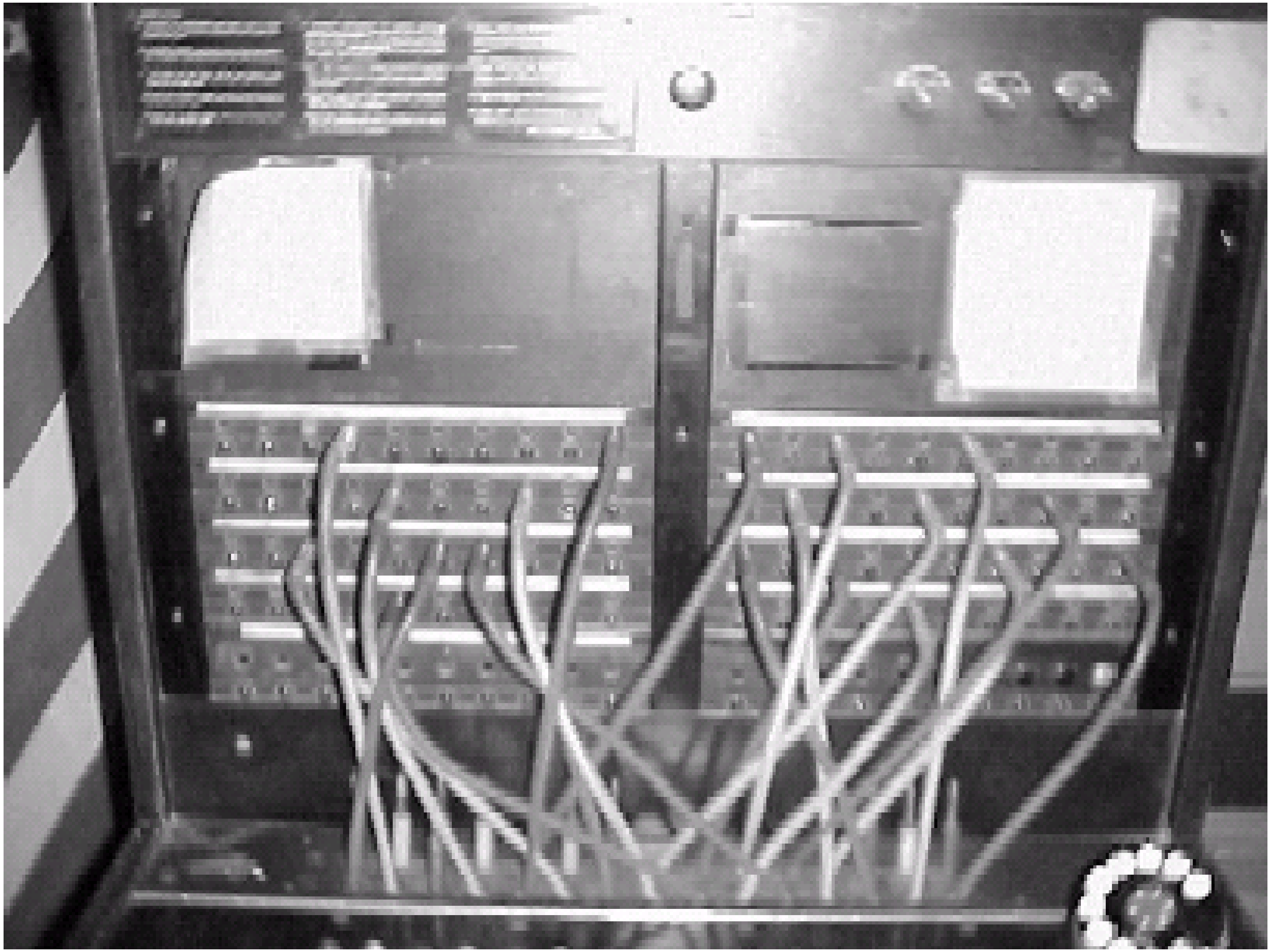


Regular Folding Chain
(Adjacent Re-entry)

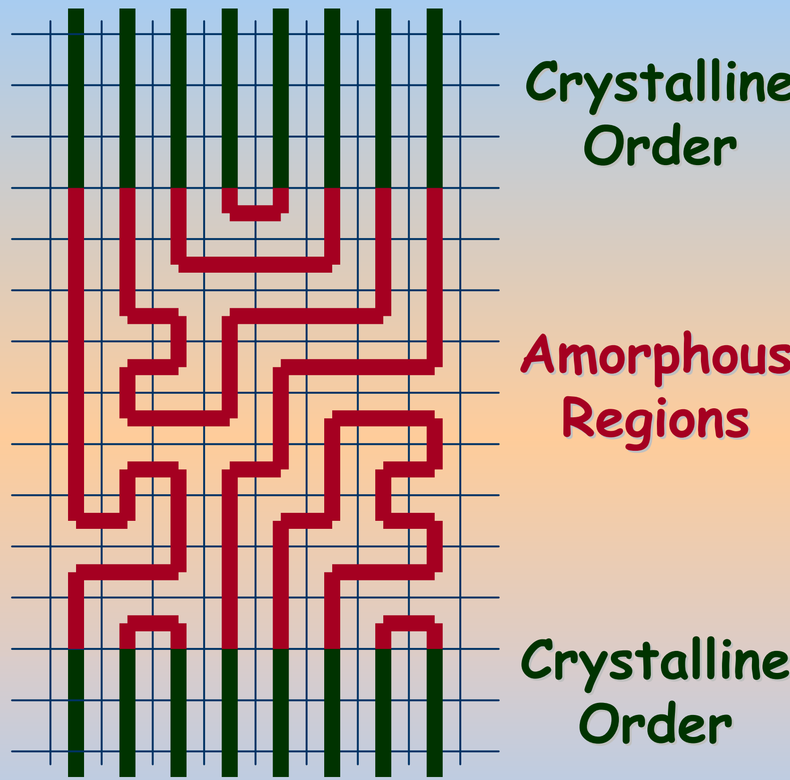


Irregular Chain Folding
(Random Re-entry)

The Flory Switchboard Model

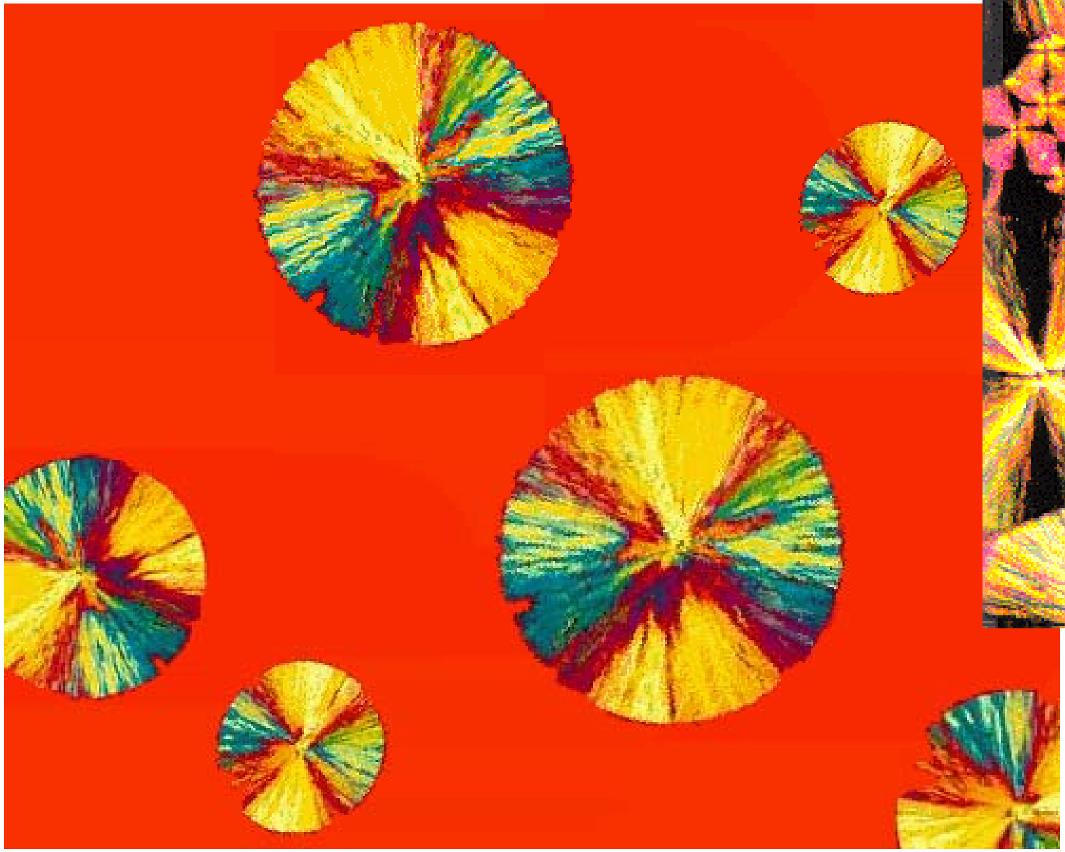


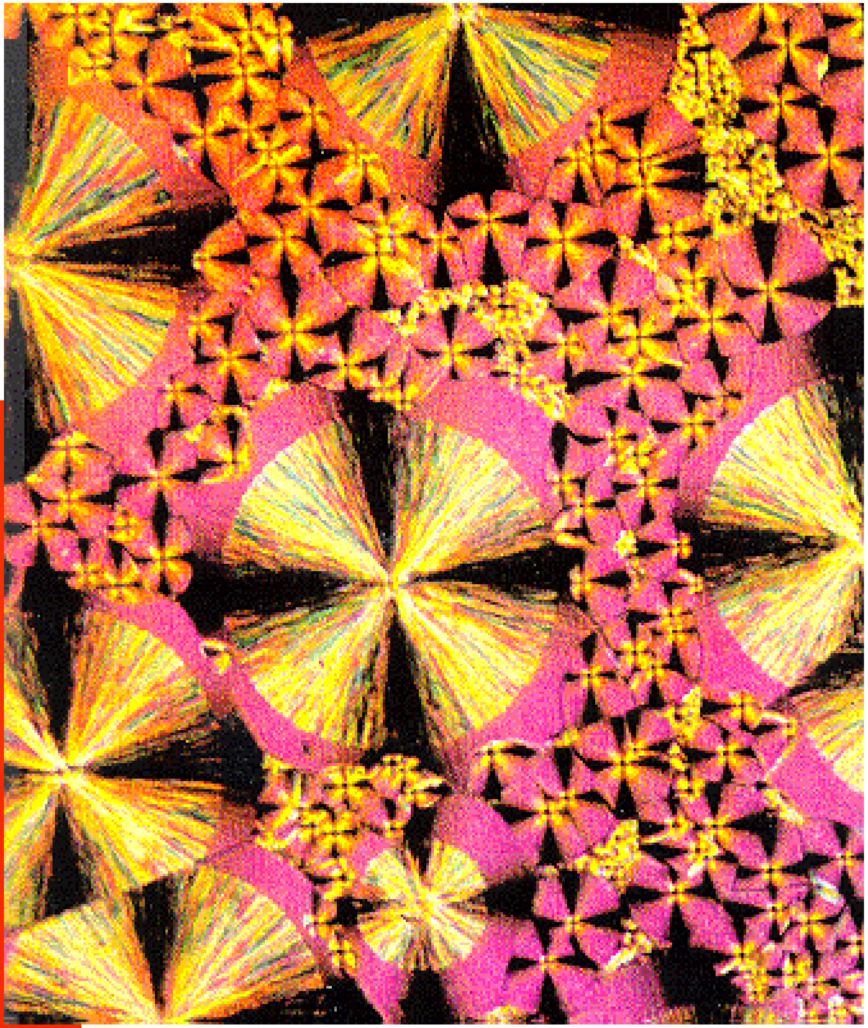
Flory Strikes Back!



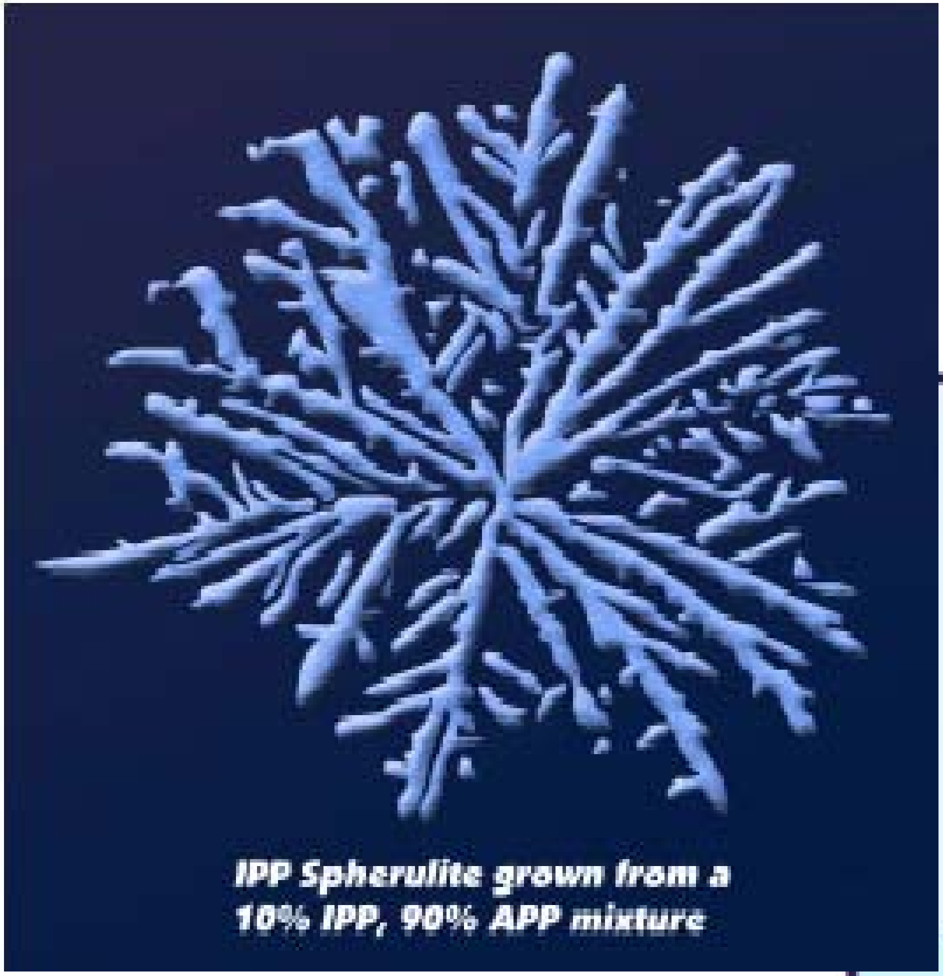
Redrawn from K. A. Dill and P. J. Flory,
Proc. Nat. Acad. Sci., ***77****, 3115 (1980).*

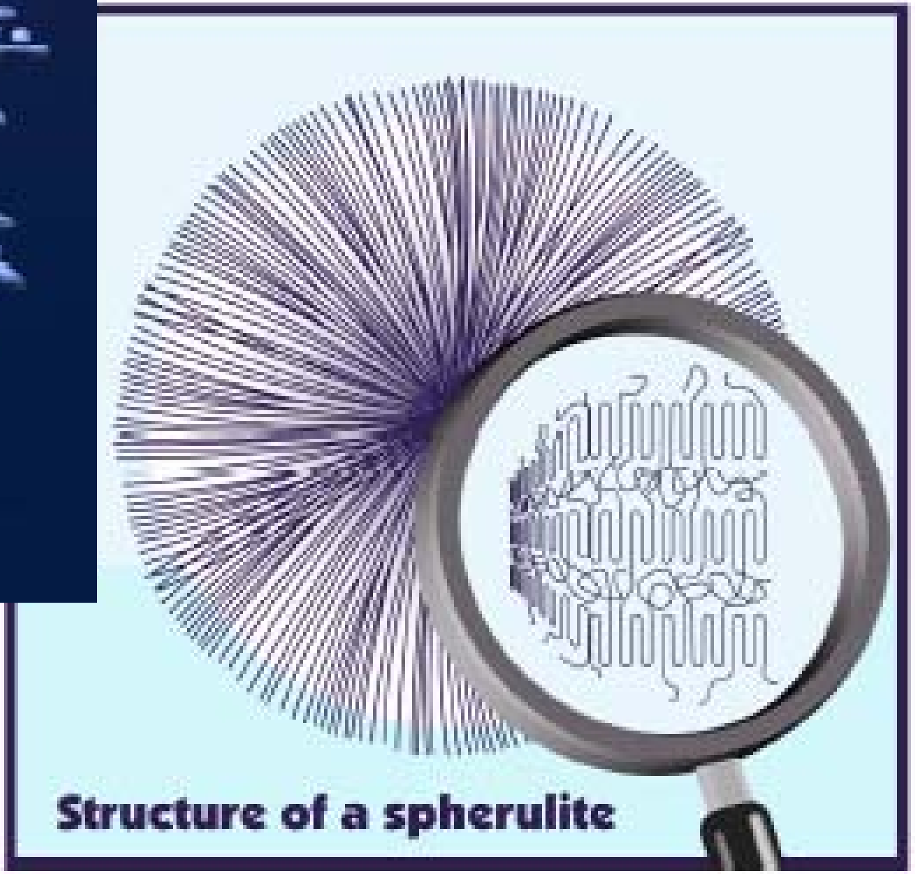
Spherulites



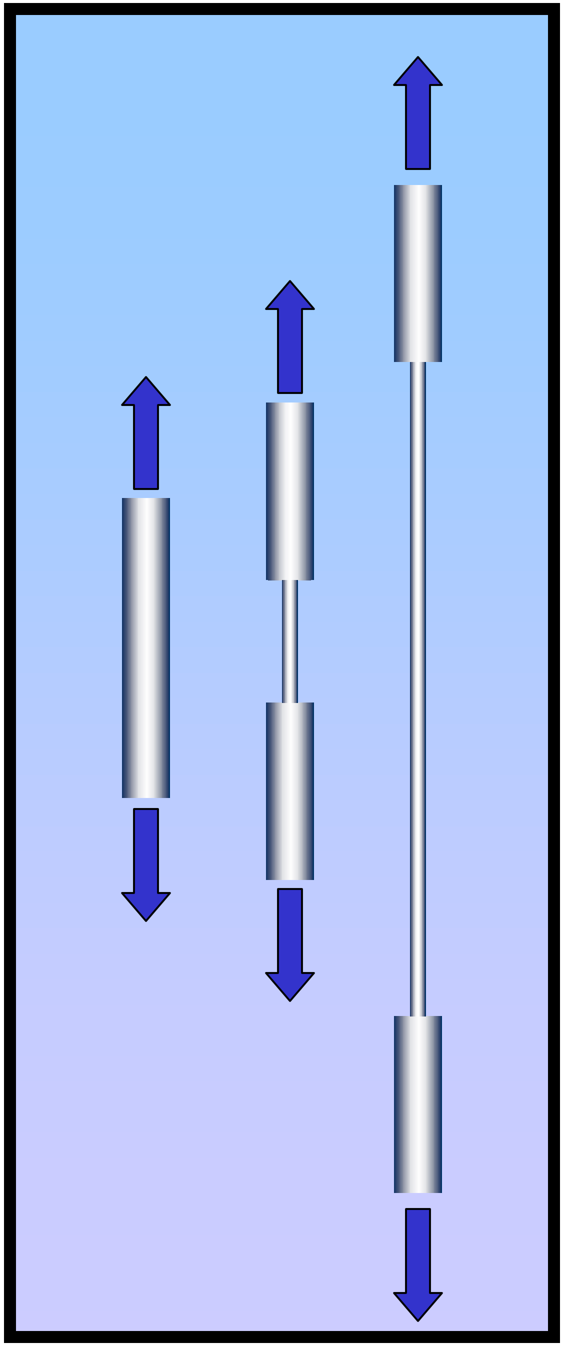


Spherulites

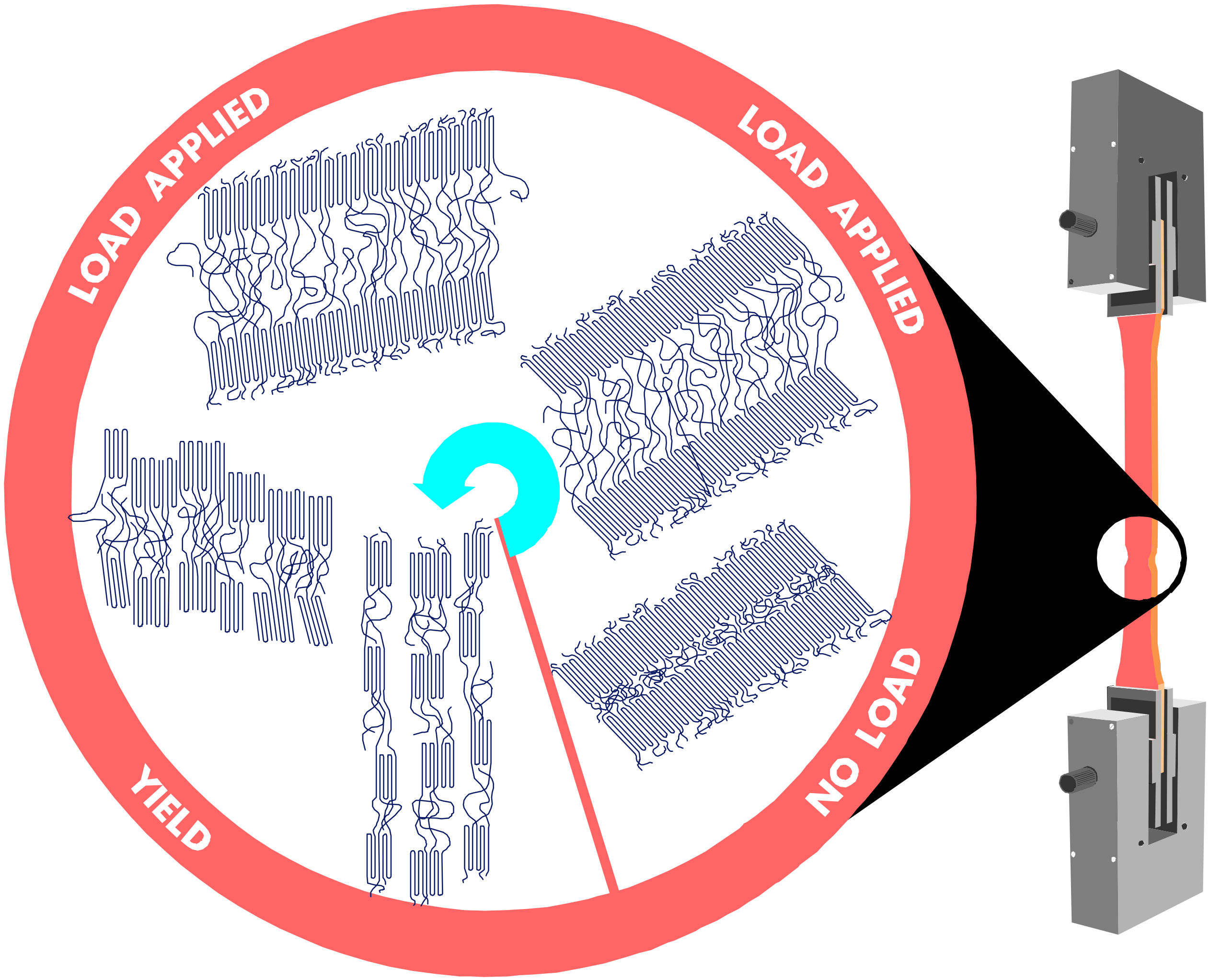




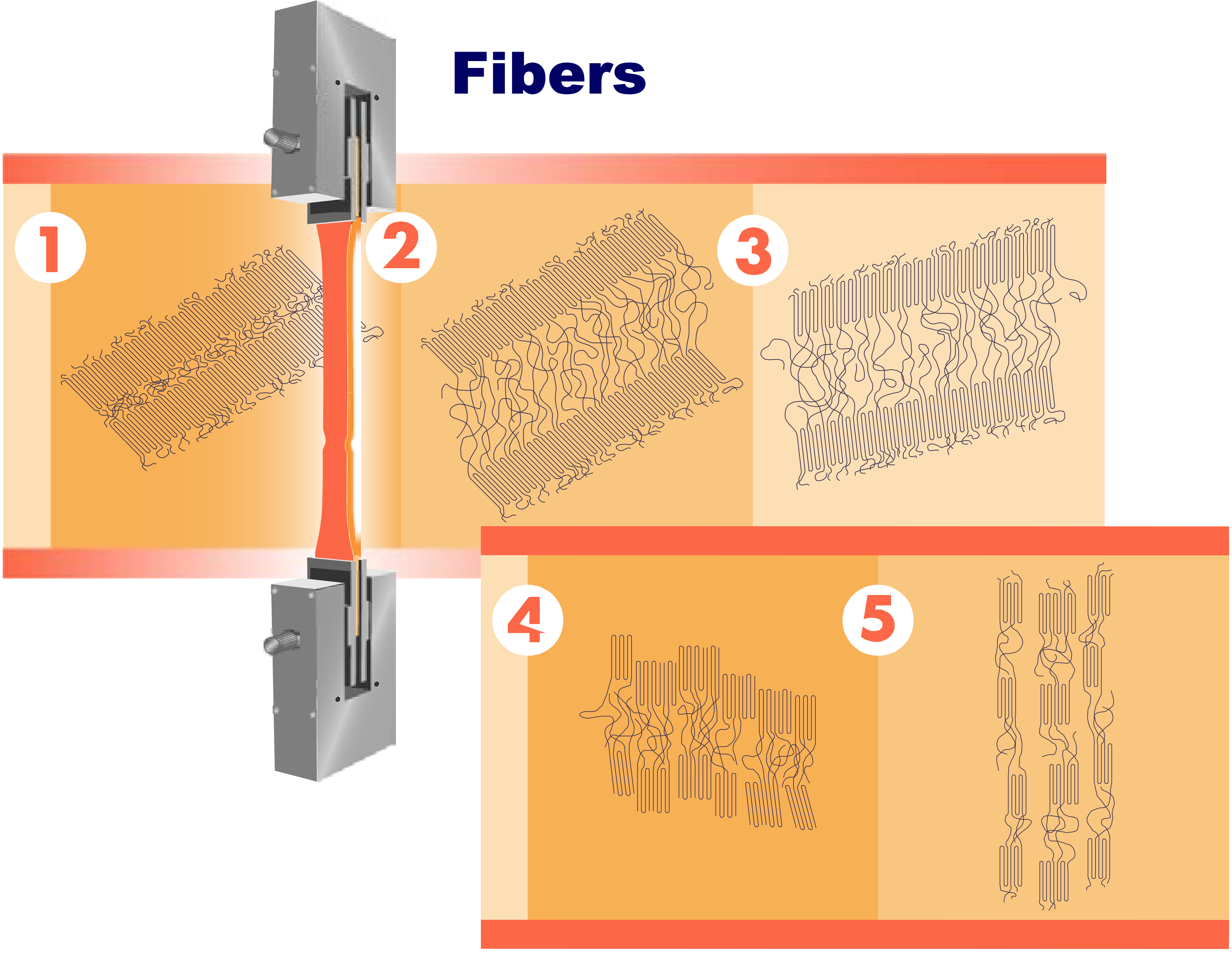
Fibers



Fibers



Fibers



What we would like to get

Property	Change with Increasing Degree of Crystallinity
Strength	Generally increases with degree of crystallinity
Stiffness	Generally increases with degree of crystallinity
Toughness	Generally decreases with degree of crystallinity
Optical Clarity	Generally decreases with increasing degree of crystallinity.Semi-crystalline polymers usually appear opaque because of the difference in refractive index of the amorphous and crystalline domains, which leads to scattering. Will depend upon crystallite size.
Barrier Properties	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
Solubility	Similarly, solvent molecules cannot penetrate the crystalline domains, which must be melted before the polymer will dissolve. Solvent resistance increases with degree of crystallinity