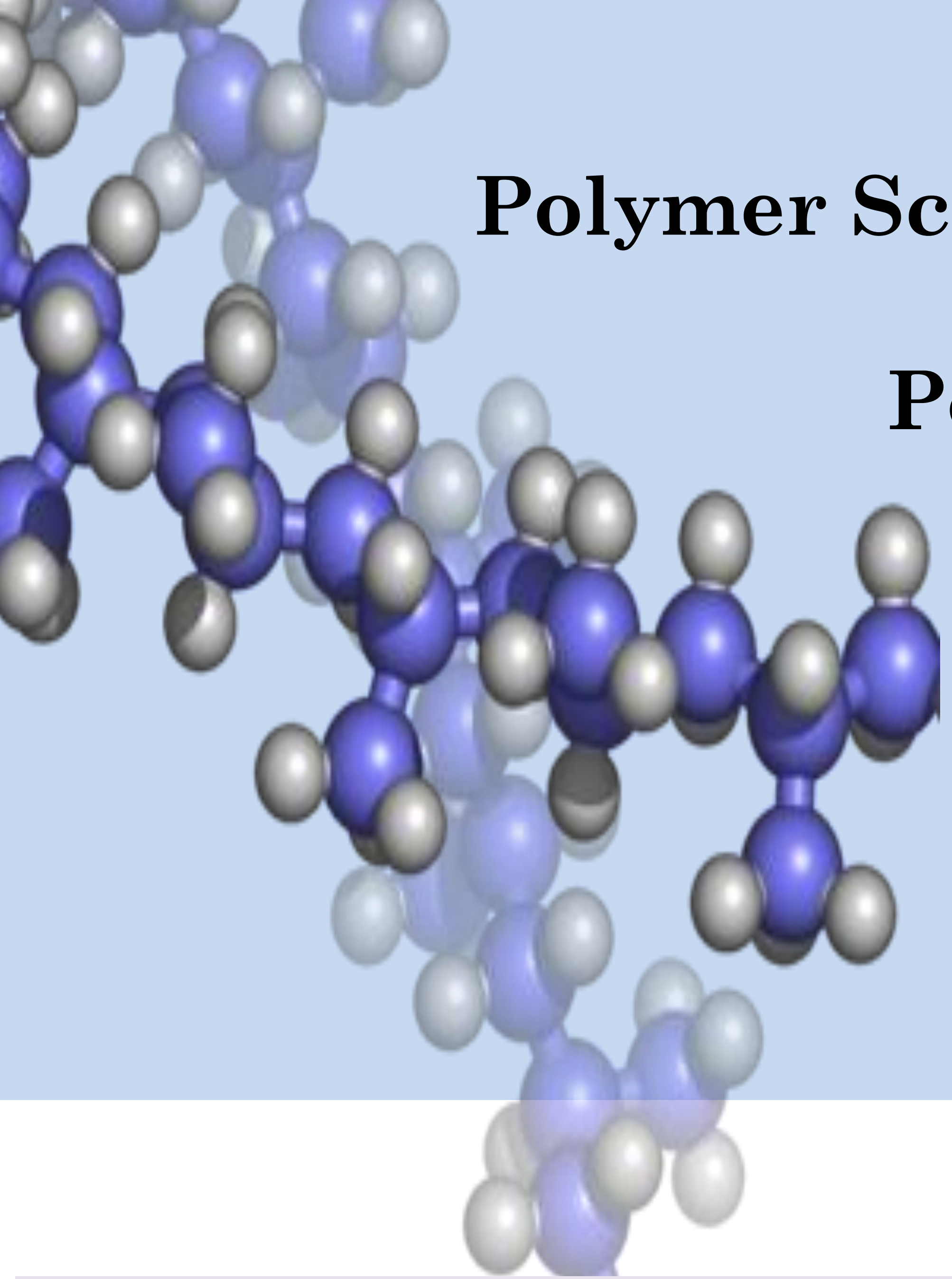

Polymer Science & Engineering

Polymers Morphology

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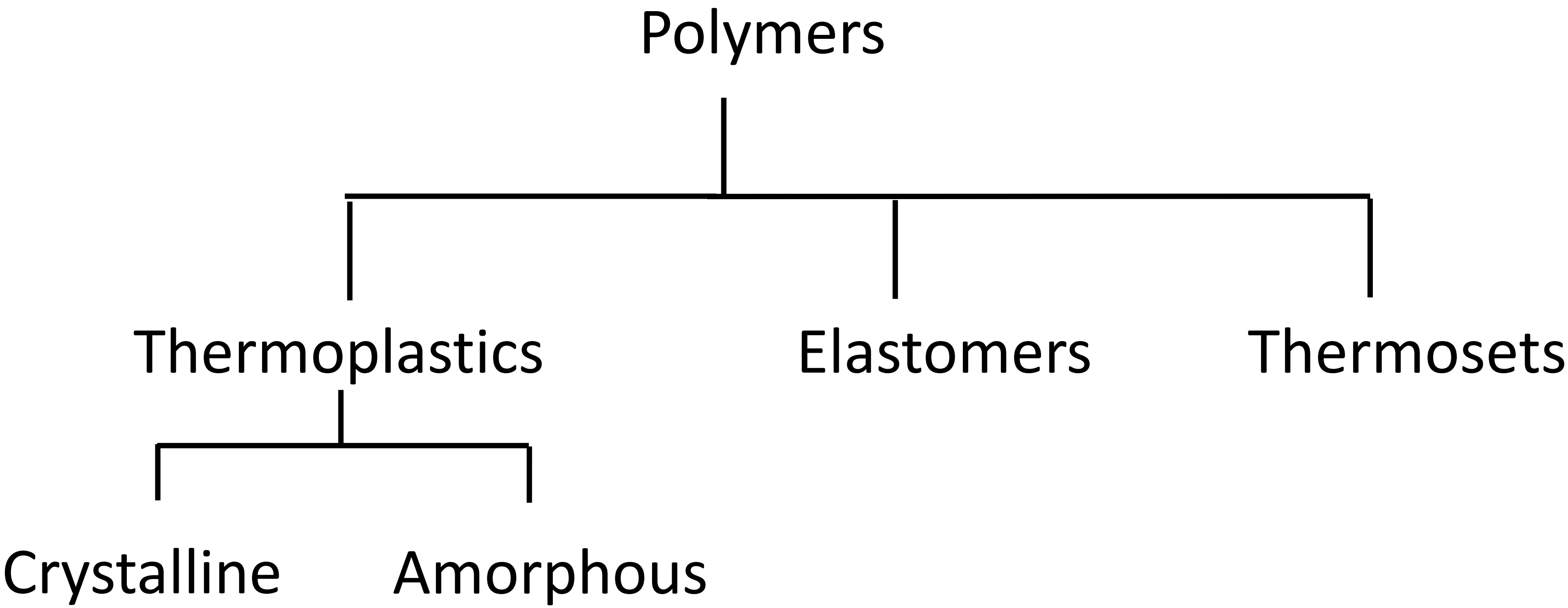
Polymers Classification



Introduction

- Thermoplastics never achieve 100% crystallinity, but instead are **semicrystalline** with both **crystalline** and **amorphous** domains.

- The crystalline phases of such polymers are characterized by their melting temperature (**Tm**).

- Many thermoplastics are completely amorphous and incapable of crystallization, these amorphous polymers (and amorphous phases of semicrystalline polymers) are characterized by their glass transition temperature (**Tg**).

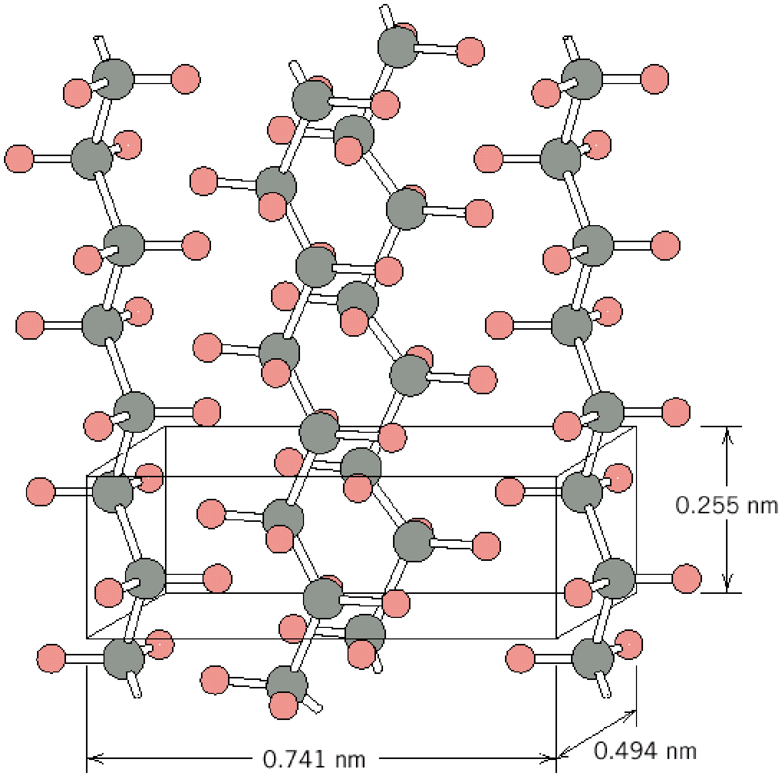
- **Tg** is the temperature at which they transform abruptly from the glassy state (hard) to the rubbery state (soft). This transition corresponds to the onset of chain motion.

  - below the Tg the polymer chains are unable to move and are “frozen” in position.

- Both **Tg** and **Tm** increase with increasing chain stiffness and increasing forces of intermolecular attraction

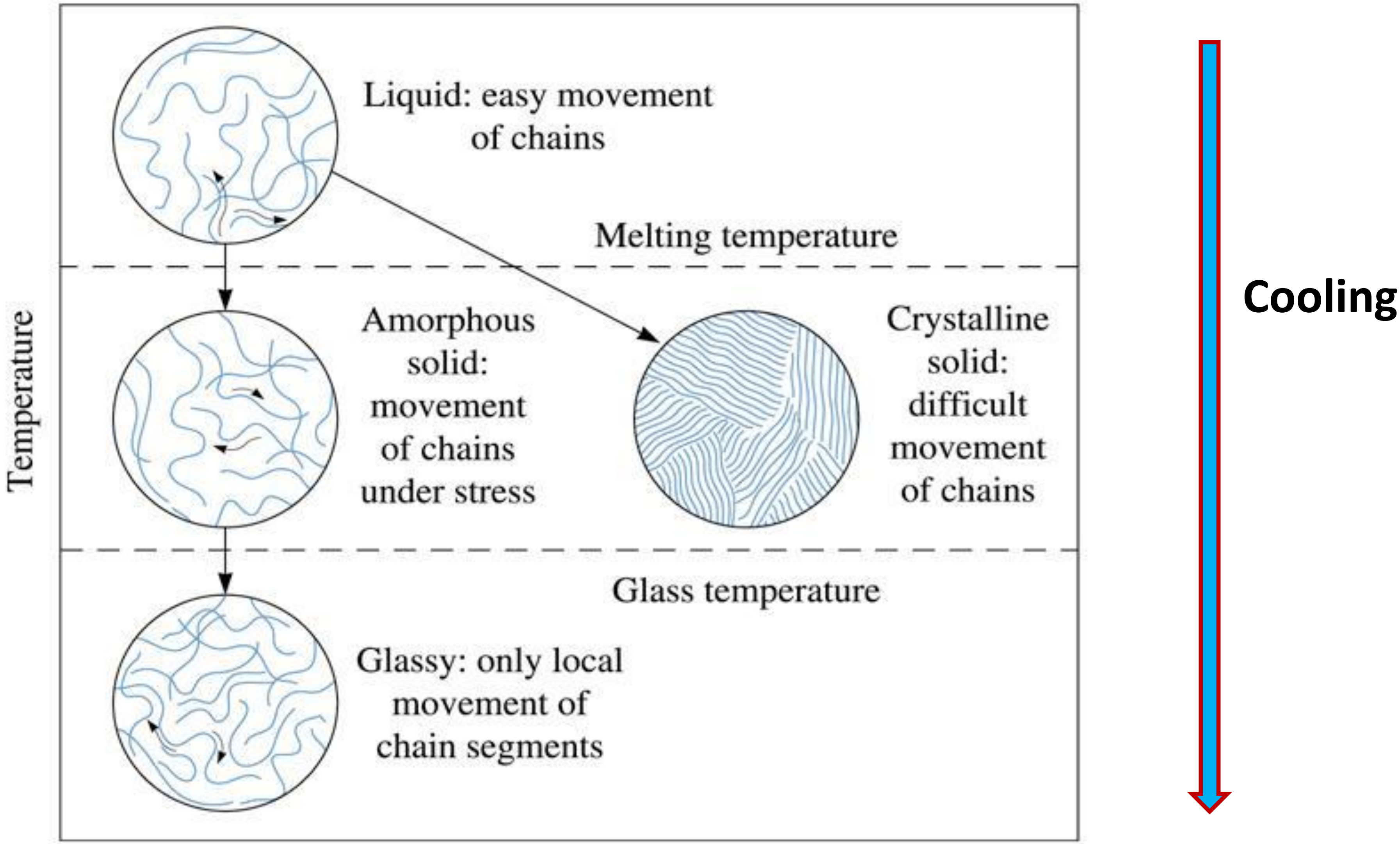
Crystallinity in Polymers

- The crystalline state may exist in polymeric materials.
- However, since it involves molecules instead of just atoms or ions, as with metals or ceramics, the atomic arrangement will be more complex for polymers.
- There are ordered atomic arrangements involving molecular chains.
- Semi-crystalline materials have a much sharper melt temperature range.
- Semi-crystalline materials require more energy to melt. You have to melt the crystals
- Side groups, secondary branching, and cooling rate all affect the degree of crystallinity of the final product
- Crystalline materials tend to be more chemically resistant



polyethylene unit cell.

The effect of temperature on the structure

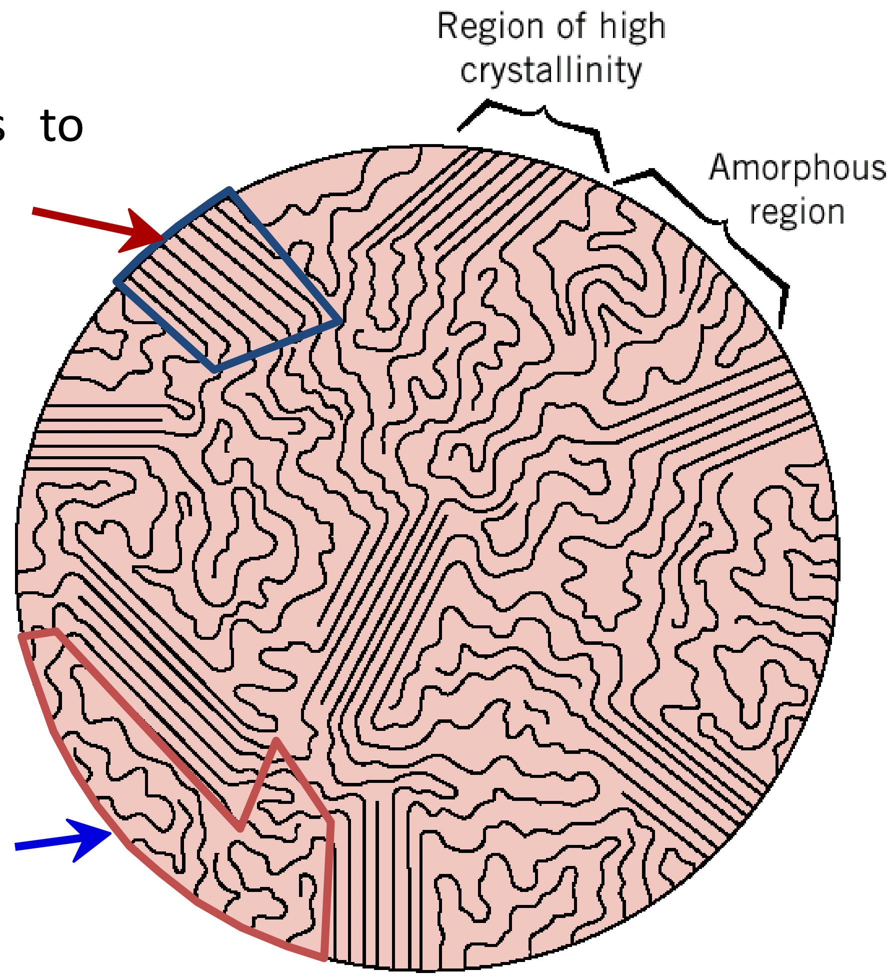


Polymer Crystallinity

➢ Polymers are rarely 100% crystalline

- Difficult for all regions of all chains to become aligned

crystalline region



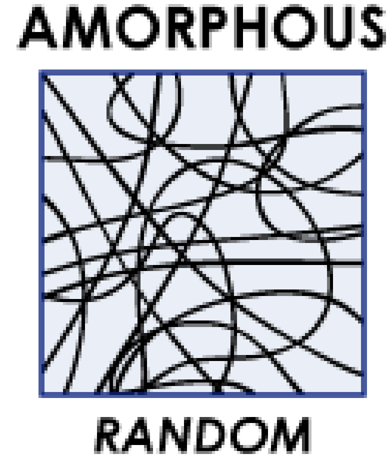
- Degree of crystallinity expressed as % crystallinity.

-- Some physical properties depend on % crystallinity.

-- Heat treating (annealing) causes crystalline regions to grow and % crystallinity to increase.

amorphous region

Amorphous Polymer



Examples: (PC, PS, PVC, PMMA, ABS)

Generally

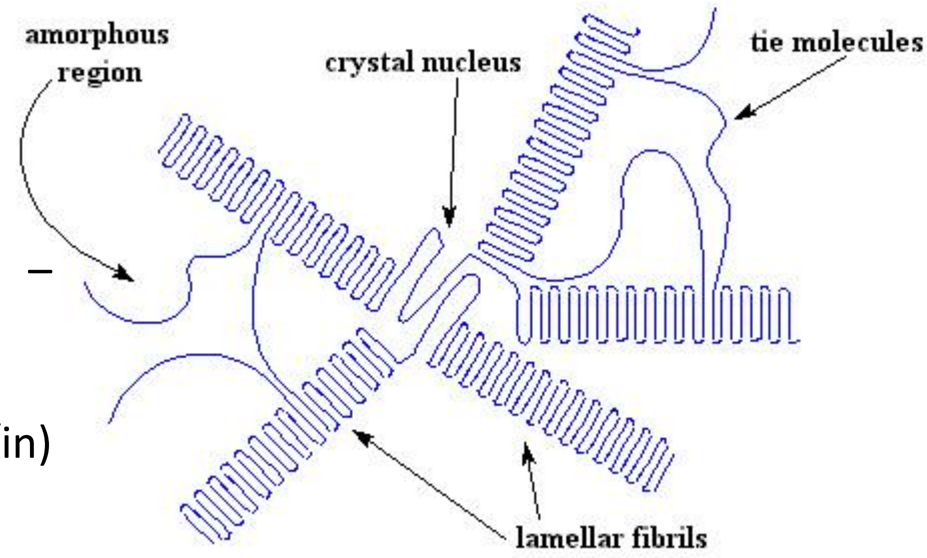
- Higher viscosity than semi-crystalline (s/c) materials – harder to make flow
- Shrink less than s/c (0.005-0.007 in/in)
- Don’t have a true melt temperature – soften more above Glass Transition Temperature – Tg
- Less chemically resistant than s/c
- Clearer than s/c (can be translucent/optical quality).
- Better weather resistance vs. s/c
- Better creep vs. s/c

Semi-crystalline polymers (s/c)

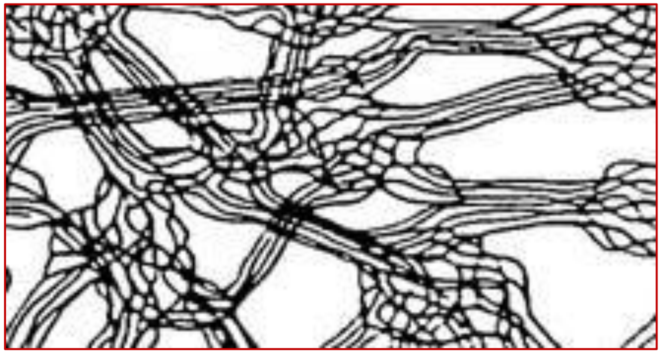
Examples: (PE, PP, PA, PET, POM)

Generally

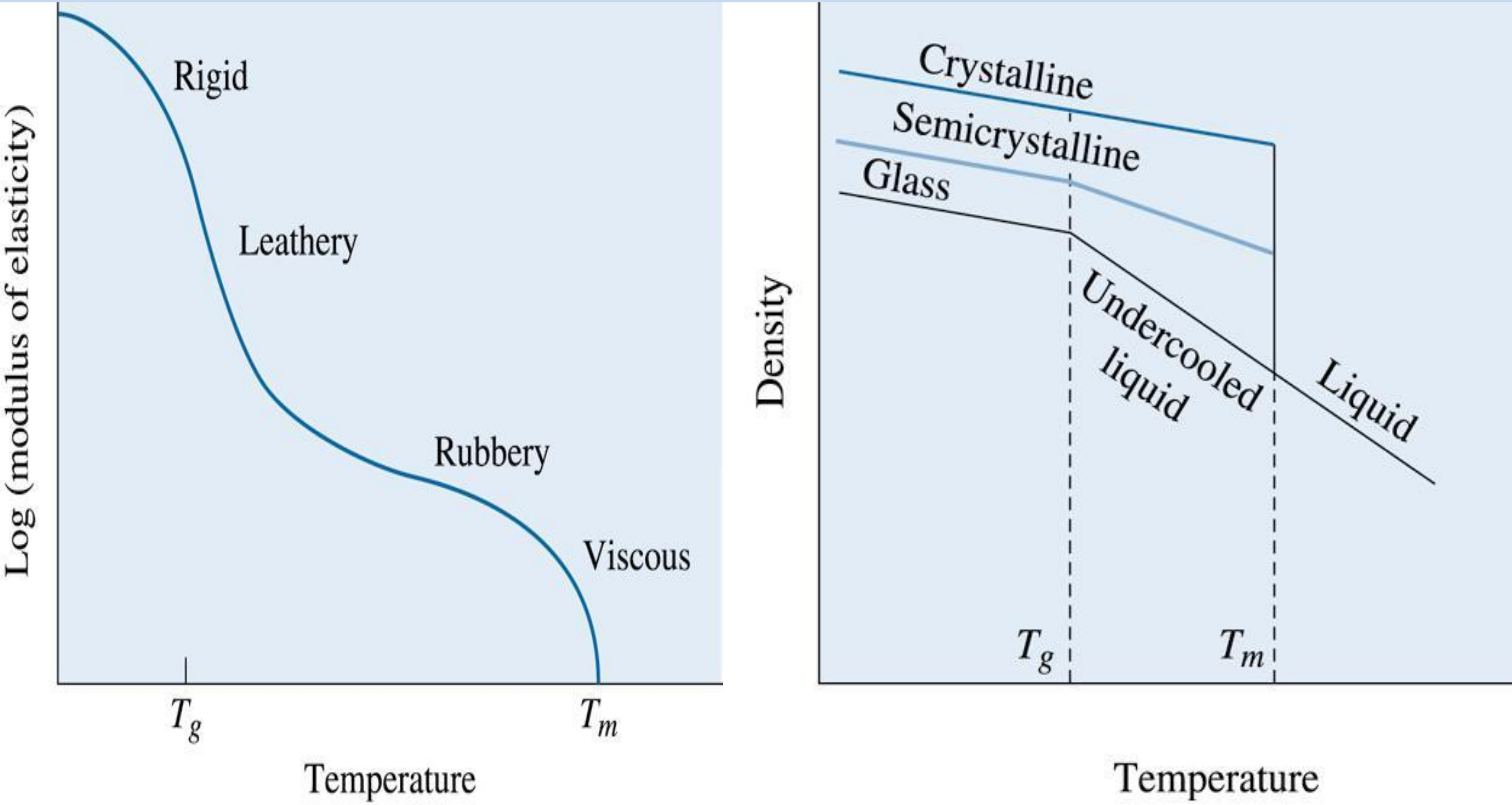
- Lower viscosity than amorphous materials – flow easier – allows them to form crystals
- Wide range of shrinkage values (.008-.050 in/in) – depends on degree of crystallinity
- Have a clearly defined melting point and a Glass Transition Temperature – Tg
- Usually translucent to opaque
- More brittle than amorphous

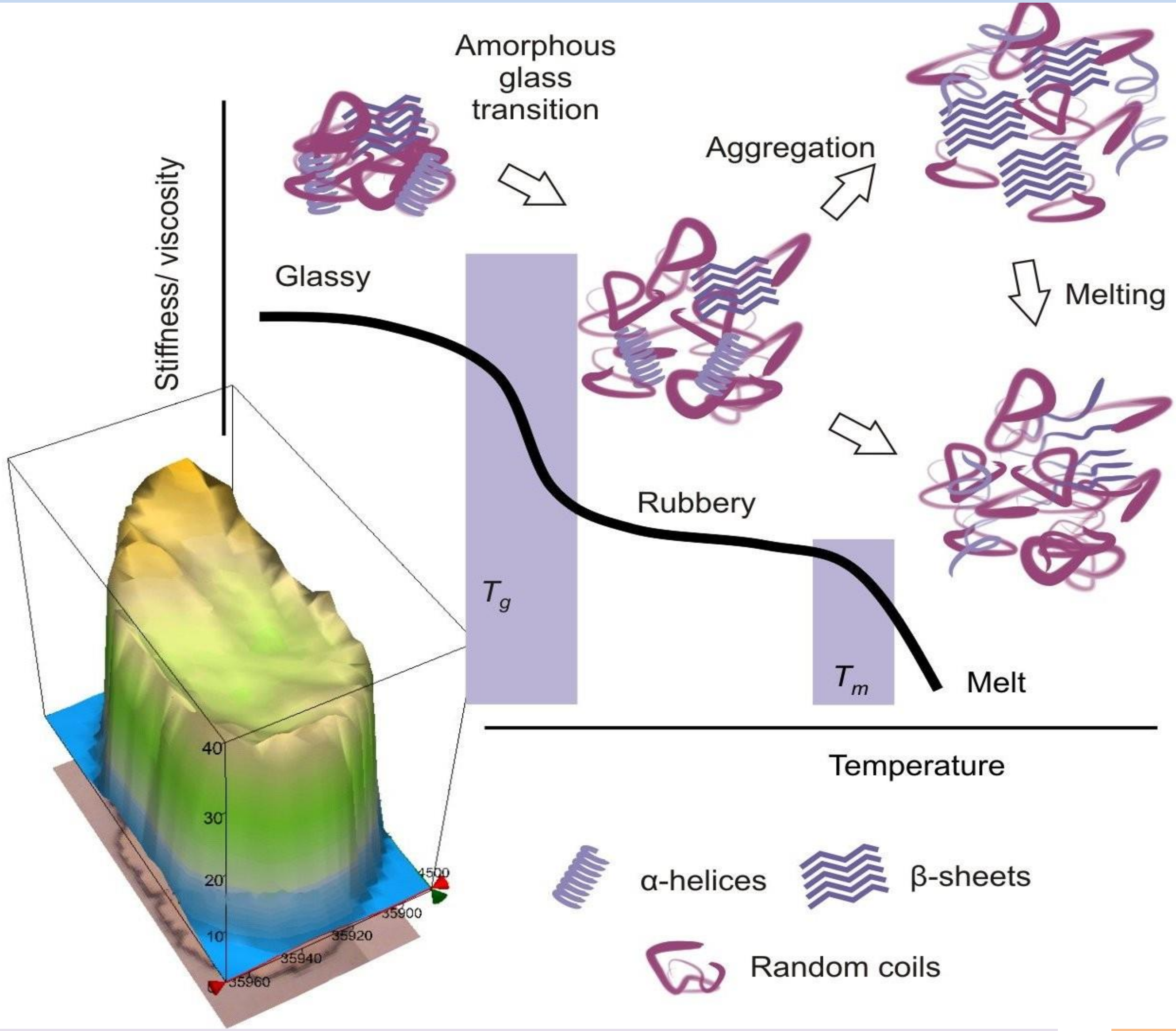


a polymer crystalline spherulite



Polymer morphology: Density & E: Effect of Temperature

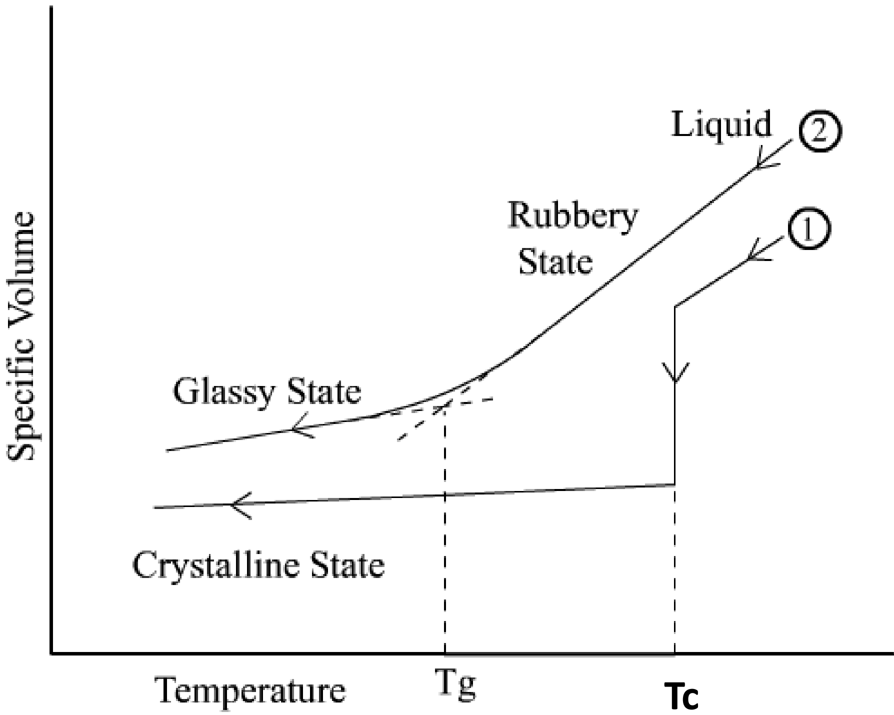



Amorphous
glass
transition
Aggregation
Melting
Stiffness/ viscosity
Glassy
Rubbery
T_g
T_m
Melt
Temperature
α-helices
β-sheets
Random coils
40
30
20
10
4500
35900
35920
35940
35960

Effect of Temperature on Sp. Volume

Depending on the polymer, there are two possibilities:

(1) polymers with irregular molecular structure (atactic PS, atactic PP, PMMA) solidify keeping their disordered microstructure and forming a stiff but brittle amorphous solid called polymer glass; the specific volume-temperature slope changes in a continuous fashion at the specific temperature of the transition and for this reason it is called glass transition temperature, Tg;



(2) polymers which have a regular structure at the molecular scale (PE, PEO, isotactic PP, isotactic PS, PA, PTFE, PETP) crystallize (partially) forming a semi crystalline material in an abrupt manner at a characteristic temperature called crystallization temperature, Tc.

For polymers, the crystallization temperature might differ from the melting temperature, Tm, by several degrees. Usually Tc < Tm.

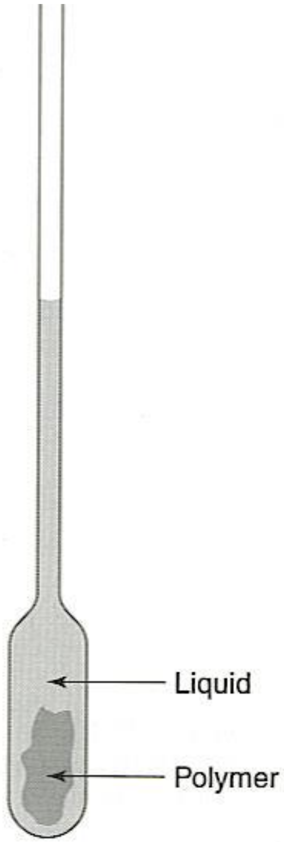
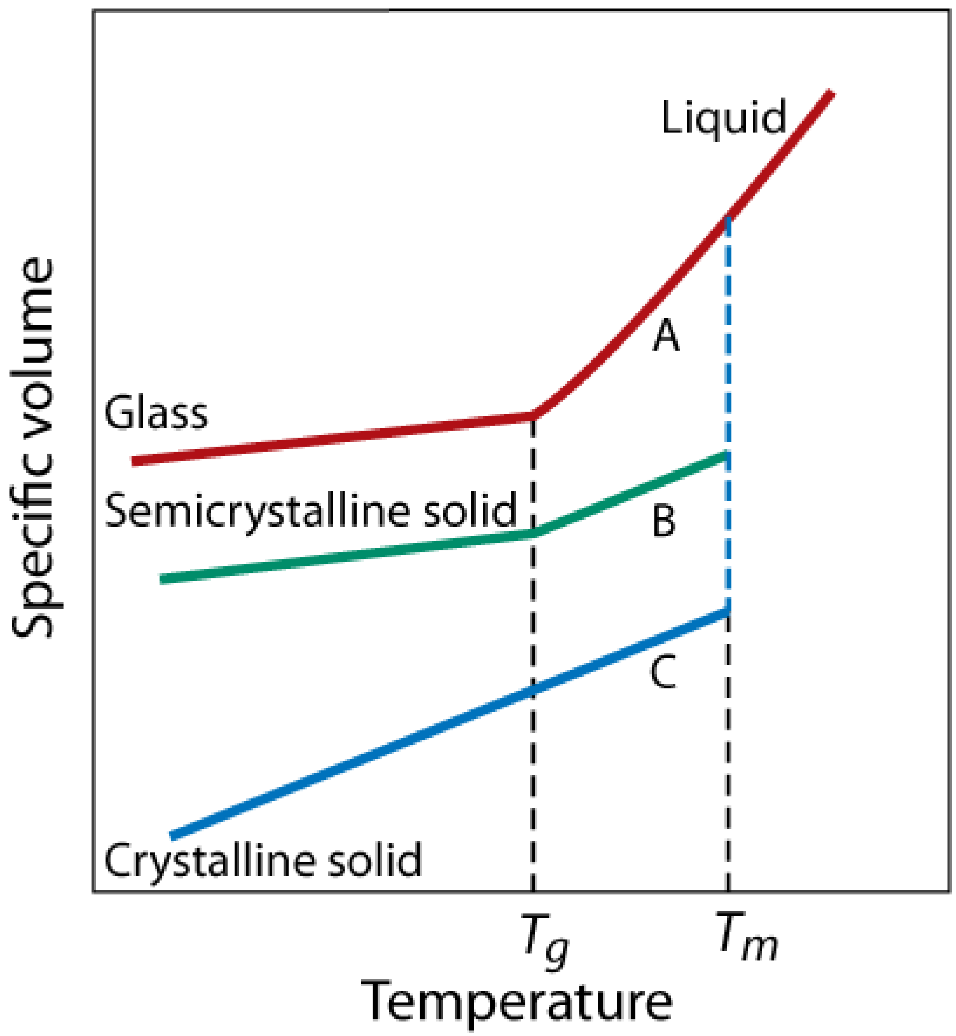
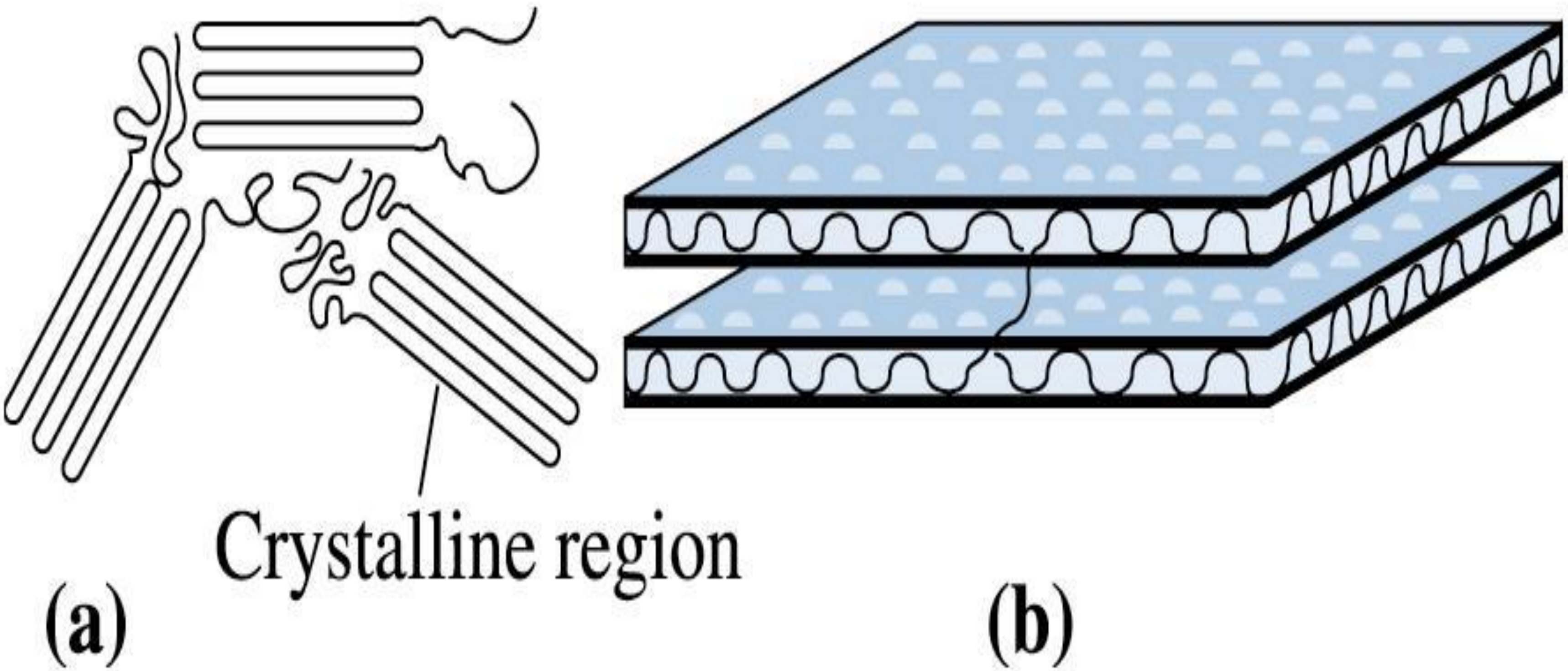


Figure 17.13 Dilatometer, used to monitor the change in volume of a polymer plus the surrounding liquid as a function of temperature by changes in the height of the liquid level in the capillary tube. Because the liquid does not undergo sharp transitions when heated, but the polymer does, any abrupt increase or changes in the slope of volume versus temperature may be attributed to T_m or T_g transitions, respectively, in the polymer.



Types of Crystallinity



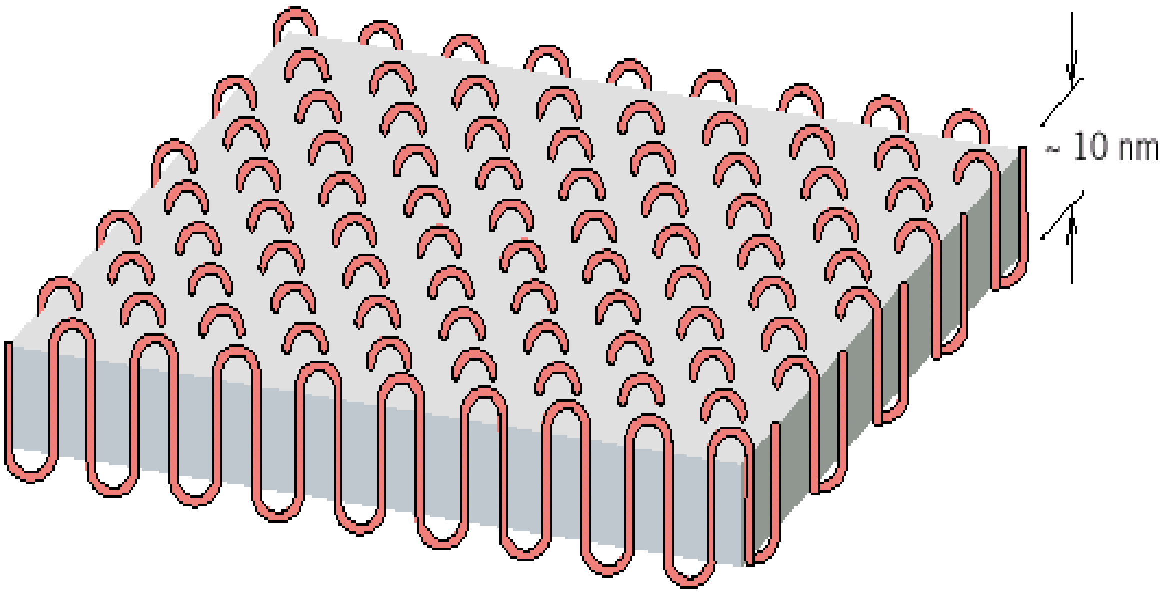
The folded chain ,model for crystallinity in polymers, shown in (a) two dimensions and (b) three dimensions.

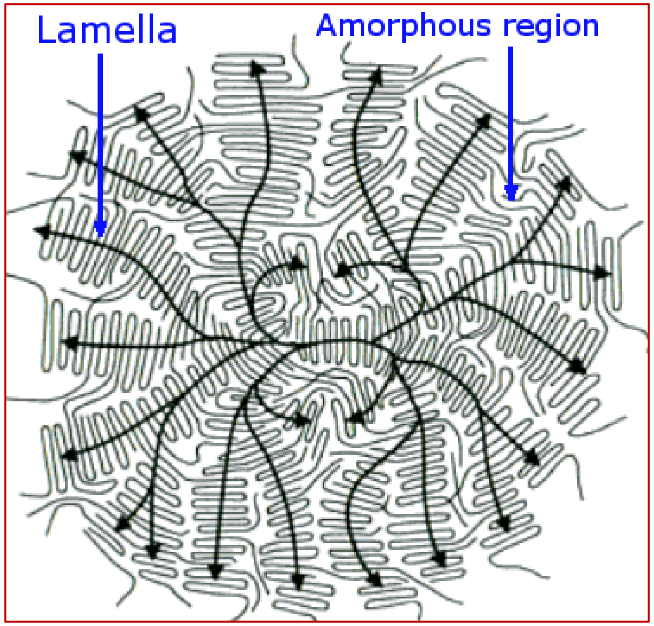
Chain folded structure

Ex: polyethylene unit cell

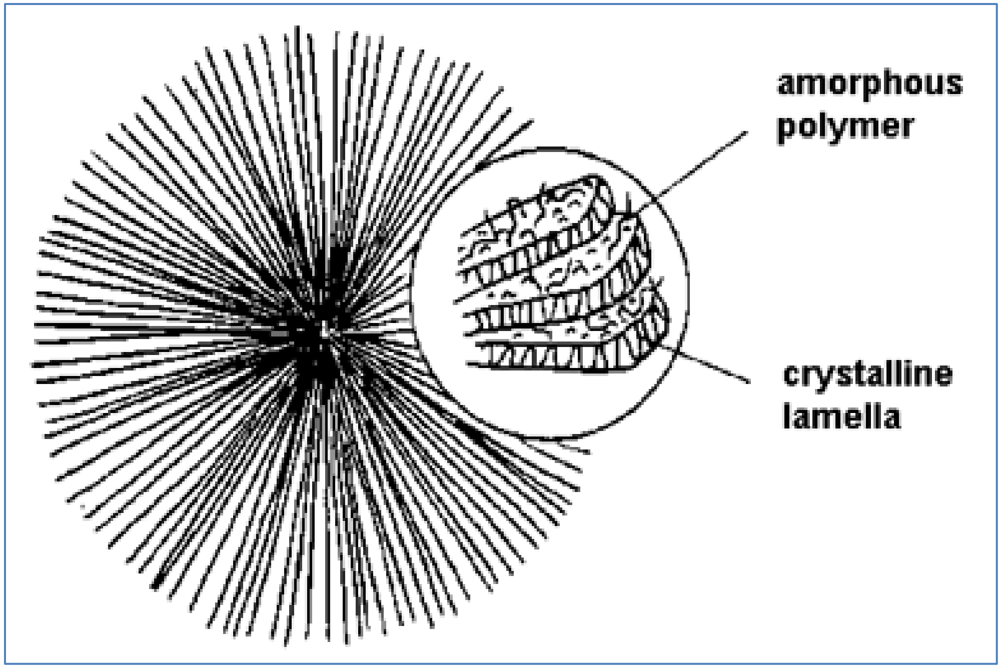
- Some polymers tend to 'fold up' and form densely packed regions in at least a portion of the polymer matrix. (>35% crystallized = Semi-crystalline)

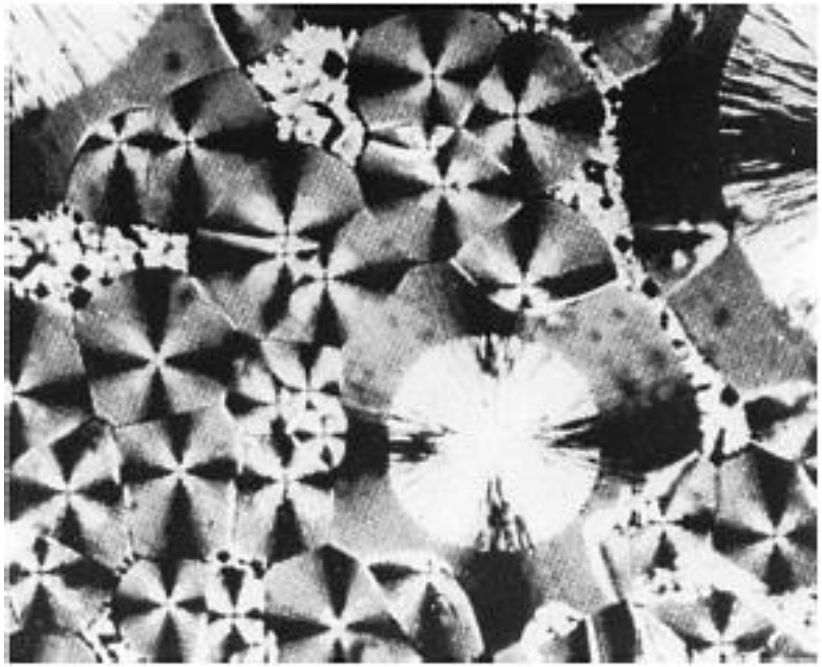
- Crystals must contain the polymer chains in some way





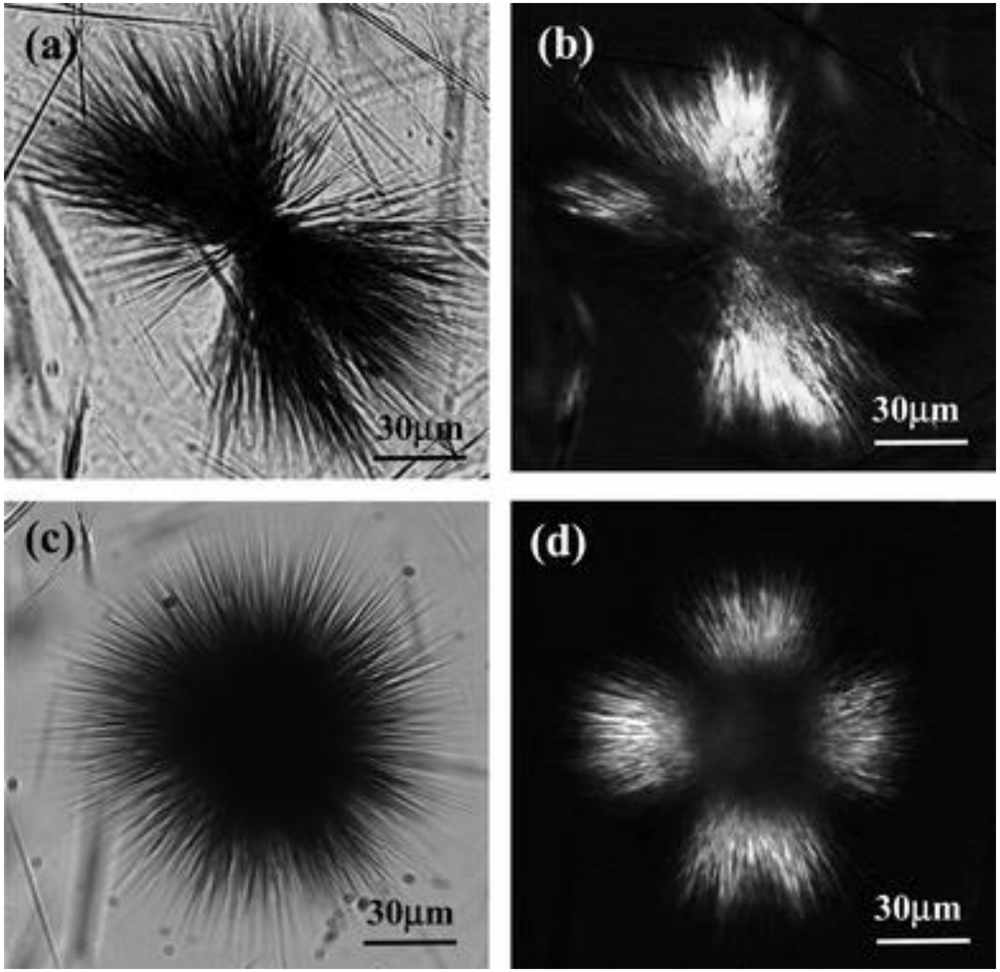
Spherulite Structure

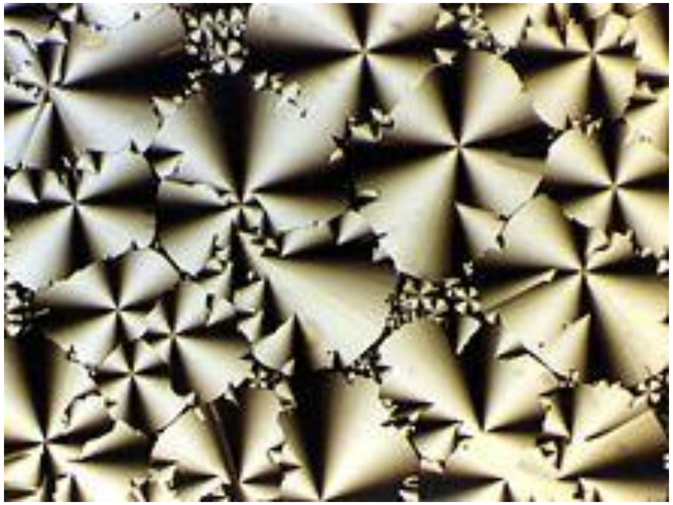


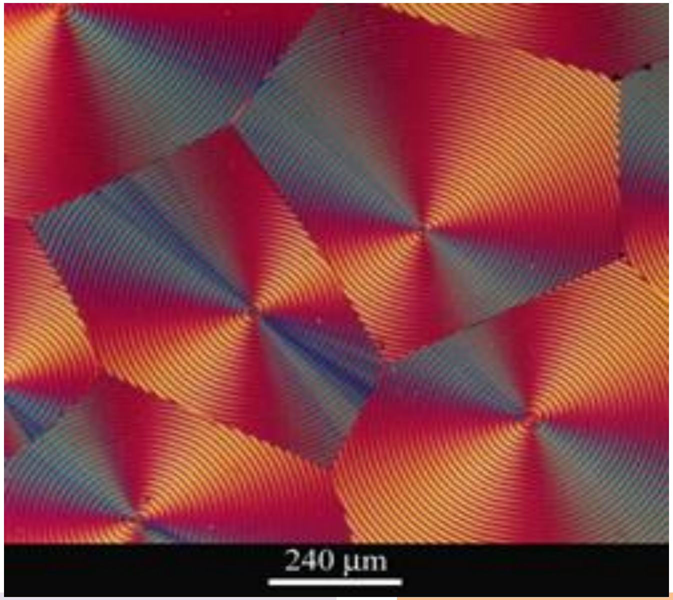


Photograph of spherulitic crystals in an amorphous matrix of nylon (× 200). (*From R. Brick, A. Pense and R. Gordon*, Structure and Properties of Engineering Materials, *4th Ed., McGraw-Hill, 1977*.)

Spherulite

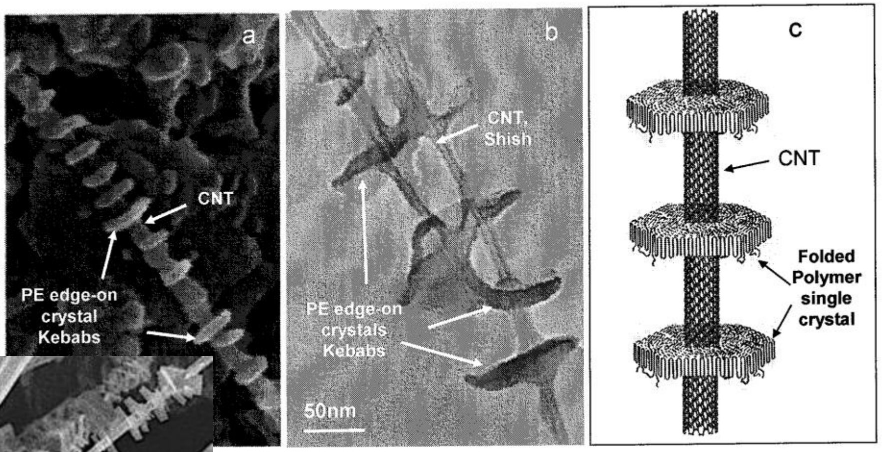


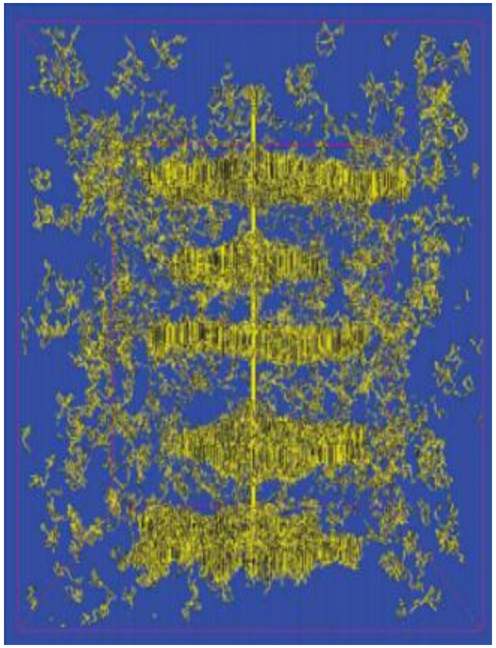


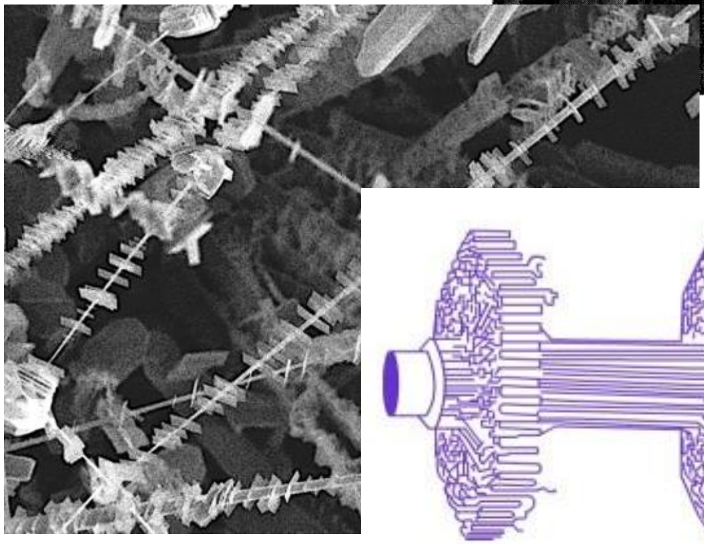


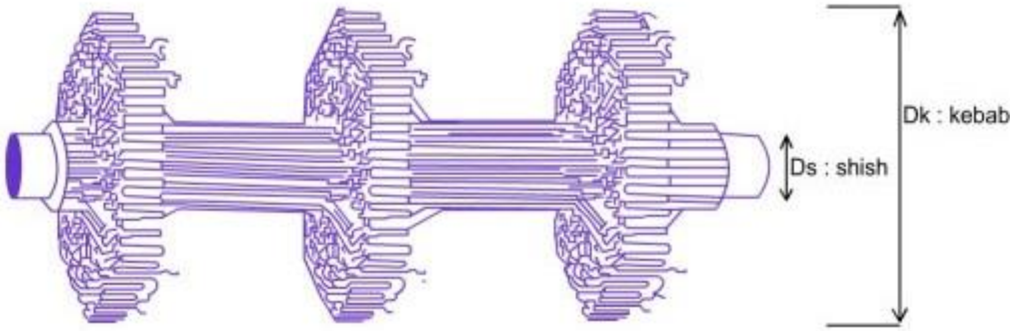
Shish-Kebab Crystalline shape

When polymers are crystallized under flows such as elongational and/or shear flows the so-called shish-kebab structure is formed, which consists of long central fiber core (shish) surrounded by lamellar crystalline structure (kebab) periodically attached along the shish.









Factors Affecting Tg

- Physical Change: Expansion of volume
- Free volume required to allow segmental motion
- Tg is proportional to Rotational Freedom
- For symmetrical polymers
  Tg/ Tm in °K ≈1/2
- For unsymmetrical polymers
  Tg/ Tm in °K ≈ 2/3
- Crosslinking Reduces Segment Mobility

- **Tg is an approximation**
  Depends upon measurement technique
  Depends upon molecular weight
  Polystyrene MW = 4000 Tg = 40°C
  = 300,000 = 100°

Properties Affected by Tg

Specific Volume / Density
Specific Heat, Cp
Refractive Index
Modulus
Dielectric Constant
Permeability

Factors affecting Crystallization

- **Thermodynamic**

1. Symmetrical chains which allow regular close packing in crystallite
2. Functional groups which encourage strong intermolecular attraction to stabilize ordered alignment.

- **Kinetic**

1. Sufficient mobility to allow chain disentanglement and ultimate alignment

   Optimum range for mobility
   $T_m - 10^\circ \rightarrow T_g + 30^\circ$
   at Tm segmental motion too high
   at Tg viscosity too high

2. Concentration of nuclei

   concentration of nucleating agents
   thermal history of sample