Chemical Engineering 160/260
Important Concepts, Lecture 9-16

Lecture 9: Introduction to Thermodynamic Models for Polymer/Solvent (and Polymer/Polymer Mixing)

- Configurational Entropy without any chains (two species arranged randomly on a lattice)
- Ideal Solution for two species
  o $dH_{mix} = 0$
  o dS_{mix} is configurational only
  o dS_{mix} from boltzman equation
- Non-ideal situations:
  o First consider links between monomer units
  o Second consider energy interactions between monomers and solvent molecules
- Consider one species having connections between segments:
  o Derive an expression for # ways to arrange a polymer given i-1 polymers already placed on the lattice. Parameters include
     ▪ Z coordination number of lattice
     ▪ n = # lattice sites
     ▪ N = total number monomers + solvent molecules
     ▪ N_1 = # solvent molecules, N_2 = # polymer mers
     General approach: derive an expression for # ways
     Apply Boltzmann's Equation to get S_{mix}
     Apply Sterling's Law to eliminate exponentials
     Obtain entropies of pure solvent, pure polymer
     Subtract of latter quantities from S_{mix} to obtain dS_{mix}
- Non-ideal energy interactions
     o Model -> two solvent molecules and two mers interacting only with the same species now interact with the second species; calculate change in energy
     o Leads so chi parameter

Lecture 10: Phase Diagrams and Behavior

- Cohesive Energy Density:
     o Value: way to predict solubilities of polymer blends based solely on the energy of vaporization of solvents in which the polymers are miscible.
     o Can be mathematically related to dH_{mix} assuming geometric mean mixing rule.
- Phase equilibrium: dG = 0, and chemical potential of each species is the same in all phases
- Single phase regime: dG curve shows no points of inflection, concave up for all values of composition. Intercepts of each compositional axis with a line tangent to the curve at some composition give the chemical potential of each species relative to its chemical potential in the pure, unmixed state (at standard T,P) for the composition.
- When dH >0, dS <0, a "hump" can arise in the free energy of mixing curve. Then mixtures with compositions between the minima can lower their total energy by phase segregating to the compositions of the minima. Depending on its composition relative to the inflection points and the minima, a single phase solution may be unstable or metastable with respect to phase separation.

- Tracing out the compositional values of the minima and inflection points versus temperature yields a UCST type phase diagram: the polymers phase segregate for some range of compositions up to a critical temperature value, above which a single phase regime exists for all compositions.
- Use of dG_{mix} derived last time to quantify the spinodal and binodal (phase equilibrium) curves and to define the critical point
- Actual polymer behavior: LCST vs. UCST
- Spinodal Decomposition vs. Nucleation and Growth

Lecture 11: Polymer Blends

- Qualitative lecture
- Reasons for development of polymer blends
- Strategies to develop blends
- Desirable properties
- Tradeoffs between properties for some successfully developed polymer blends

Lecture 12: Block Copolymers for Molecular Architecture

- Qualitative Lecture
- Motivation for block copolymers
- Morphology as a function of xN parameter
    o x = Florry Huggins interaction parameter
    o N = copolymer degree of polymerization
    o Cylindrical, spherical, lamellar, etc.
- Crystallization of one phase in an amorphous matrix
    o Empirical relationships for lamellar thickness as a function of amorphous and crystalline block degree of polymerization
- Micelles
- Qualitative discussion of characterization techniques for block copolymers

Lecture 13: Free Radical Polymerization Techniques:
- Bulk
    o Autoacceleration, viscosity, broad polydispersity unless fractionating
    o High purity
- Solution
    o Thermal, viscosity control
    o Chain Transfer, solvent retention
- Suspension Polymerization
- Dispersion Polymerization
    o These differ on size scale (due to the nature of the surfactant/stabilizer) and in location of the initiator (in monomer for suspension, in water for dispersion)
    o Both lead to good thermal and viscosity control. Emulsion has the added benefit of independent molecular weight and kinetic chain length control via the surfactant concentration.

o   Both yield dispersions which are probably best used as is, rather than requiring elaborate purification methods.

Lecture 14: Amorphous State, Dilute Solution

- In bulk, chains behave as though there were in a theta solvent: second virial coefficient = 0, (neutron scattering studies)
- Simple rheology: storage and loss elastic moduli, effects of oscillation frequency on the relative magnitudes of these moduli
- Dilute solution dimensional analysis (see attached table)
- Definition of c* and v* as mass/volume concentrations at which chains first begin to overlap.

Lecture 15: Amorphous State, Semi-Dilute and Concentrated Solutions

- Continued scaling analysis (see table) for *semi-dilute* and *concentrated* solutions.
- Analysis of *high concentration* via the reptation model, where movement of the polymer occurs like a snake moves, shifting its contour along its own axis. The same sorts of dimensional analysis are applied with a new length scale, the contour length of the polymer.
- Screening was introduced: when polymer chains overlap (*semi-dilute case*), beyond an effective length ξ the polymer cannot see the rest of its length. Thus polymers in concentrated solutions can be characterized by this "screening length". We looked at a more realistic model where we used the term blob to describe the portion of a polymer between any two contact points with other polymers. An entire chain can then be described by N_{blob} such blobs. We used this concept to derive an expression for the radius of gyration and saw that this value shrinks with increasing concentration relative to being in a solution of a good solvent.

Lecture 16: Semicrystalline Polymers

- General configurational requirements for a polymer to crystallize
- Polyethylene and polypropylene unit cells
- Helical structures: in crystalline solids large side groups lead to adoption of helical structures so pendant side groups are spaced in a maximum fashion.
- Hollow pyramid polyethylene crystals:
    o   Crystallographic surface planes and directions
    o   Chain Folding Models
- Spherulitic microstructure
    o   Mechanism for growth
    o   Chain conformation within a spherulite
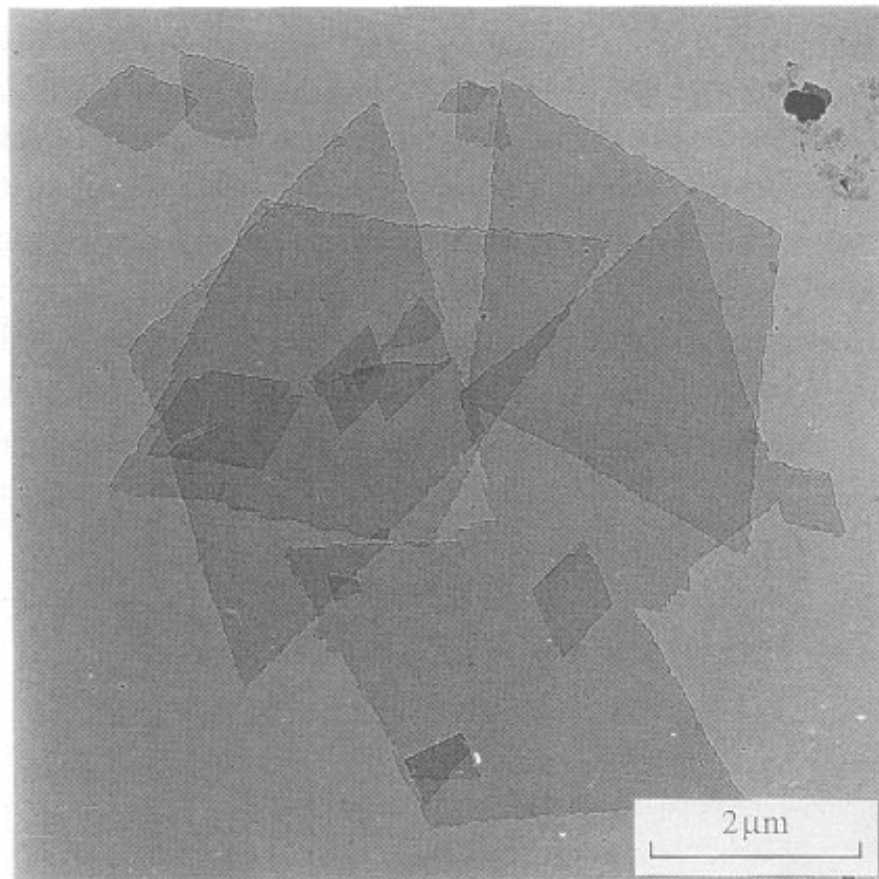   o   Impingment
    o   Tie Chains

Figure 7.11 Single crystals of linear polyethylene (BP Rigidex 140 60) crystallized from dilute solution in xylene at 74°C. Transmission electron micrograph by A. M. Hodge and D. C. Bassett, University of Reading, Reading, UK.
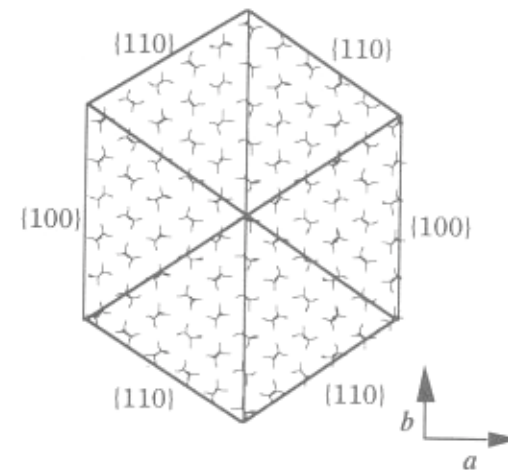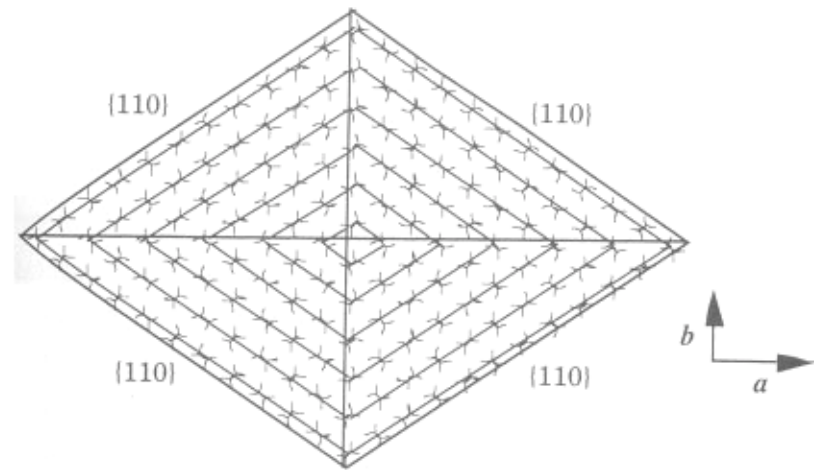

Figure 7.12 Sectorization of polyethylene single crystals. Upper crystal shows only {110} sectors whereas the lower also has {100} sectors.
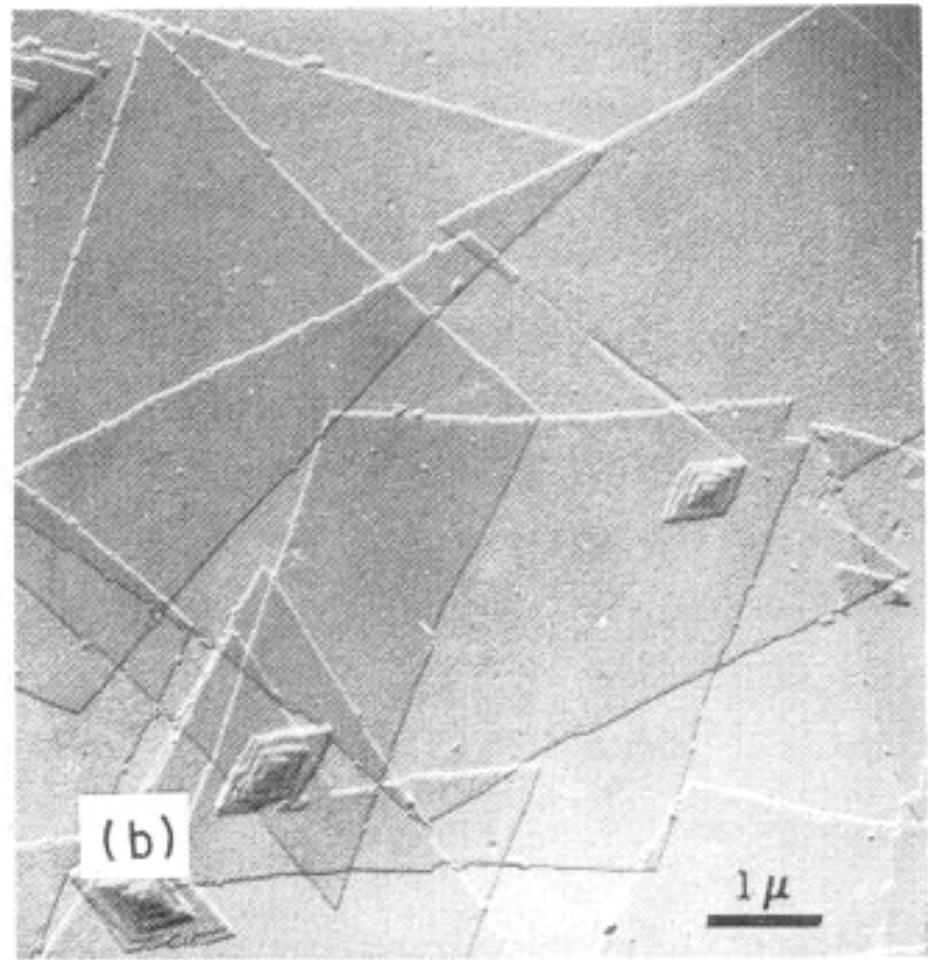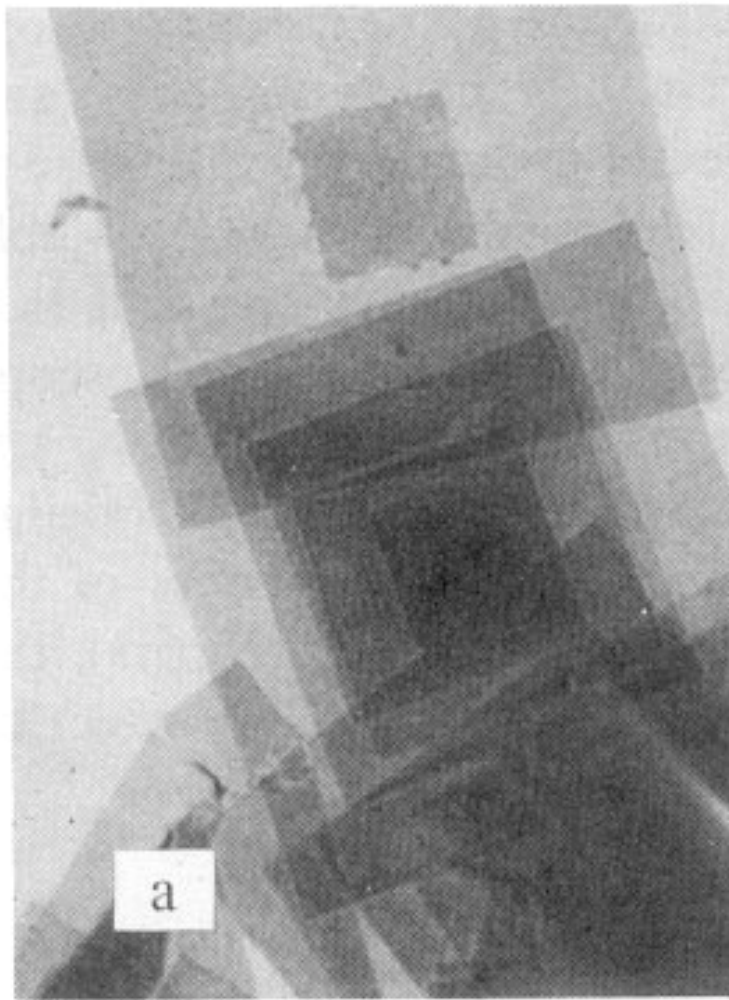
Figure 2.1. Examples of Polymer Single Crystals. (a) Poly(4-methyl-pentene-1) [D. C. Bassett et al., *Polymer*, 5, 579 (1964)]; (b) polyethylene [V. F. Holland and P. H. Lindenmeyer, *J. Polymer Sci.*, 57, 589 (1962).]
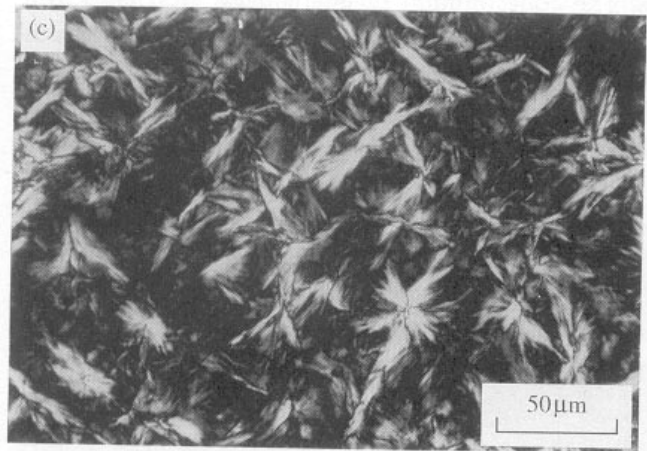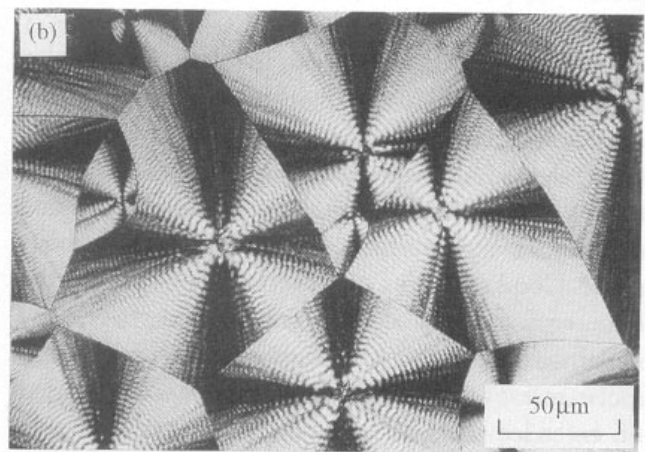
50 μm

0.5 μm

50 μm

0.5 μm

50 μm

Figure 7.27 Transmission electron micrograph showing lamellar crystals in (a) linear and (b) branched polyethylene. By M. T. Conde Braña, Dept of Polymer Technology, Royal Institute of Technology, Stockholm, Sweden.

Figure 7.34 Polarized photomicrographs of different polyolefins showing (a) non-banded spherulites (PP); (b) banded spherulites (PE); and (c) axialites (PE). Photomicrographs by S. Laihonen and U. W. Gedde, Dept of Polymer Technology, Royal Institute of Technology, Stockholm.
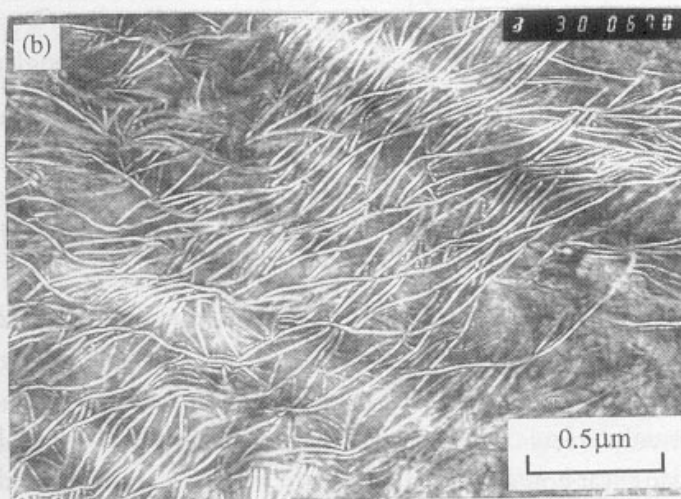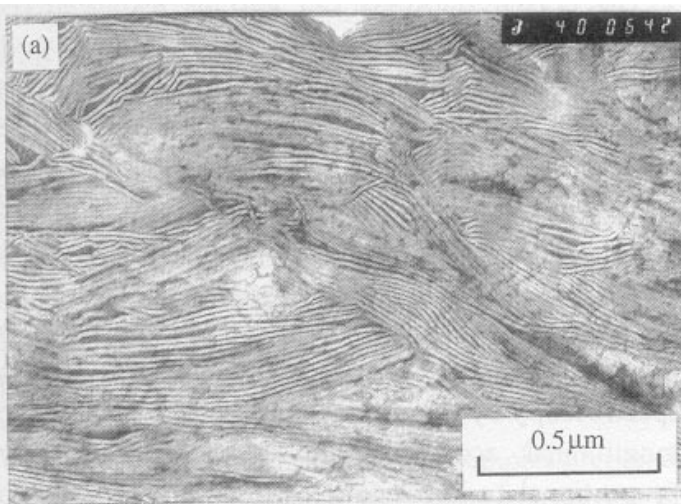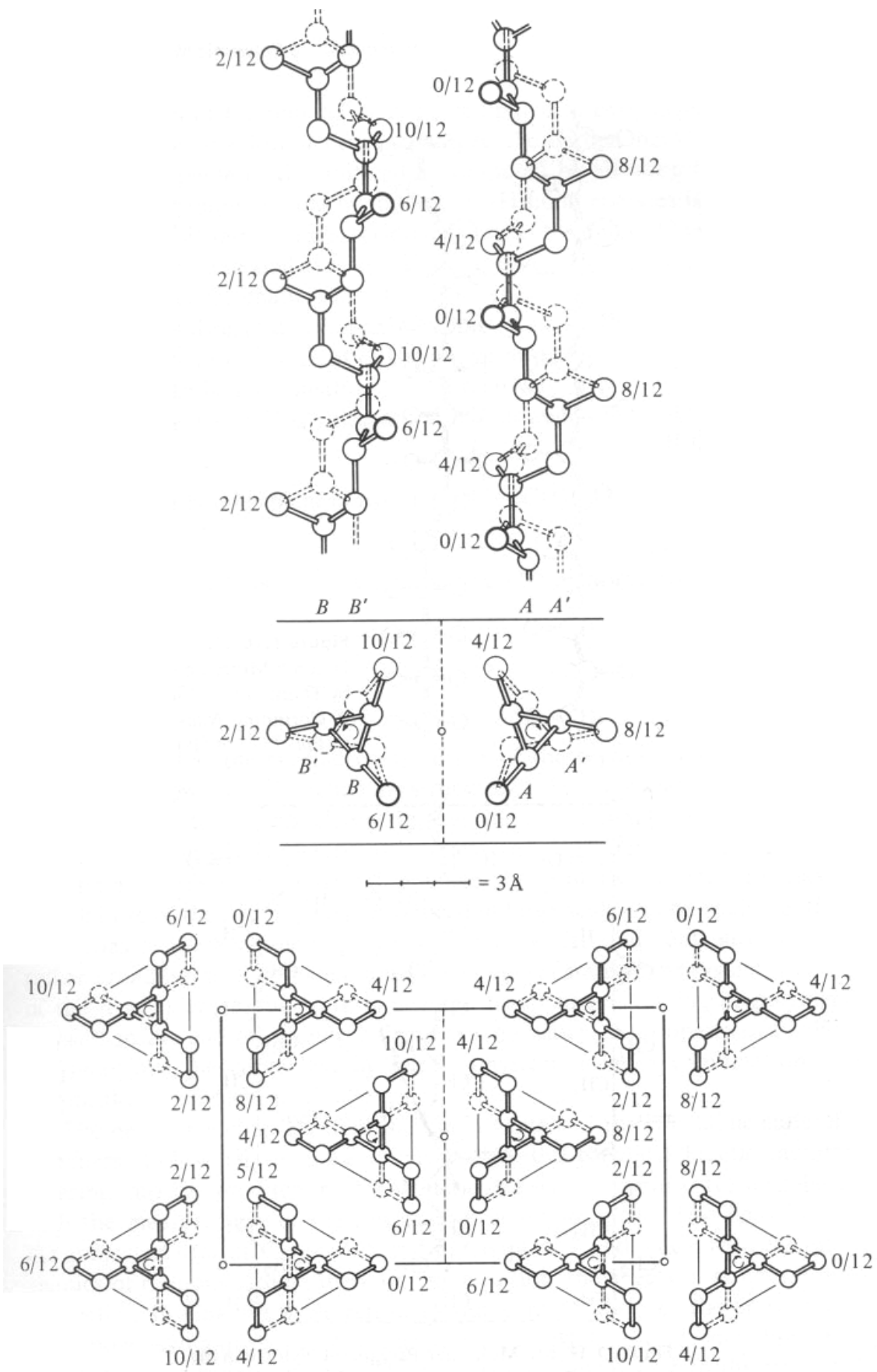
Figure 1.15. Mode of Packing of Enantiomorphic Chains in Polypropylene. [G. Natta and P. Corradini, *J. Polymer Sci.*, *39*, 29 (1959).]

Distance Scales in Crystalline Polymers

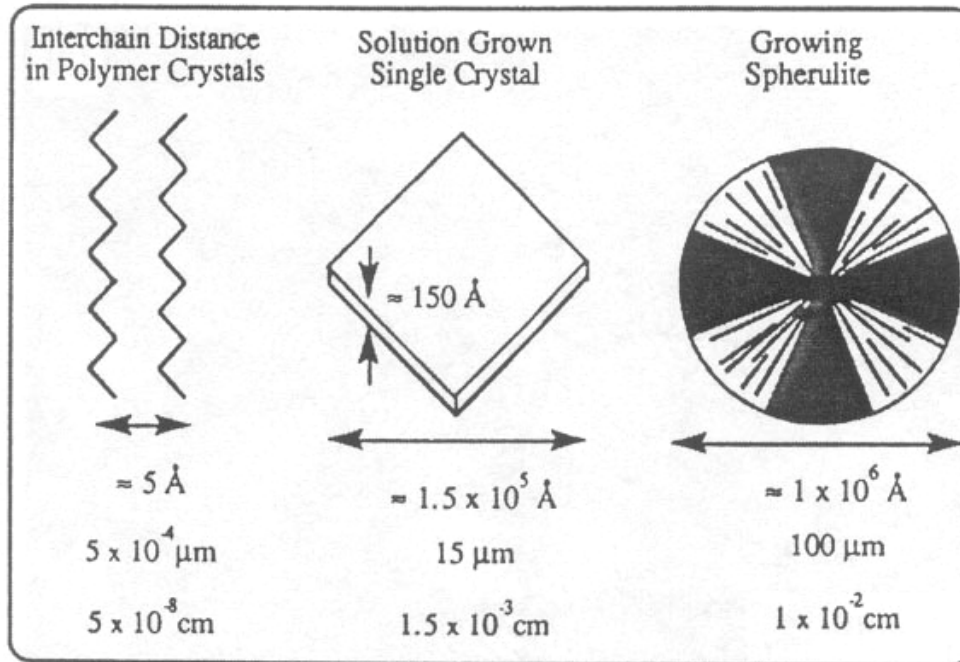| Interchain Distance in Polymer Crystals	Solution Grown Single Crystal	Growing Spherulite
$\approx 5 \text{ Å}$	$\approx 150 \text{ Å}$	
	$\approx 1.5 \times 10^5 \text{ Å}$	$\approx 1 \times 10^6 \text{ Å}$
$5 \times 10^{-4} \, \mu m$	$15 \, \mu m$	$100 \, \mu m$
$5 \times 10^{-8} \, cm$	$1.5 \times 10^{-3} \, cm$	$1 \times 10^{-2} \, cm$

Figure 7.35 A schematic representation of the size associated with various features of polymer crystals.

P.C. Painter and M.M. Coleman, p 245.

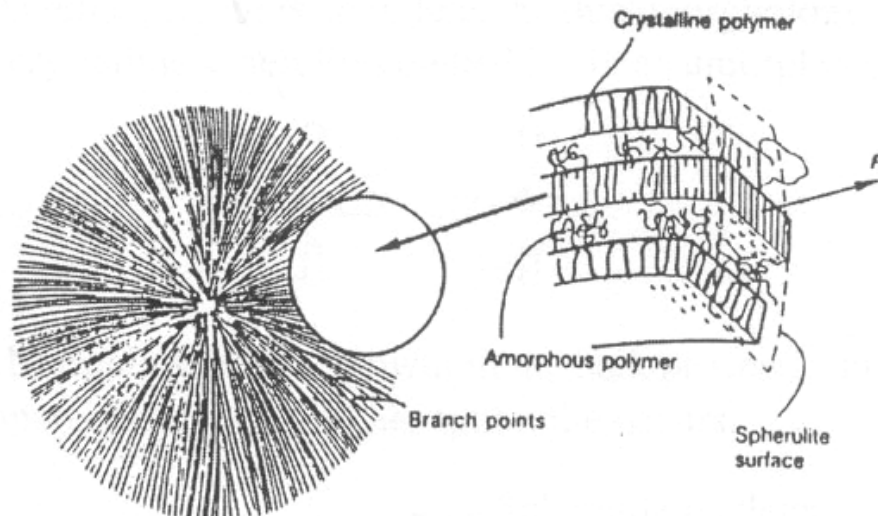# Spherulite Growth:
Amorphous and Crystalline Regions

FIGURE 11.8. Fully-developed spherulite grown from the melt, comprising chain folded lamellae (magnified section) and branching points which help to inpart a spherical shape to the structure. Most rapid growth occurs in the direction of the spherulite radius R. (Adapted from McCrum *et al.* (1988) with permission from Oxford University Press.)

J.M.G. Cowie, <u>Polymers: Chemistry and Physics of Modern Materials</u>, 1991, p 243.