Physics of Solid Polymers

Part 5

Morphology

Picture: SEM of etched surface of bulk polypropylene, showing crystal lamellae in a banded spherulite – from B. Lotz et al.

STRUCTURAL HYERARCHY IN SEMICRYSTALLINE POLYMERS

atomic scale - crystal unit cell
- several Angstroms (<1 nm to a few nm)
- detailed crystal structure, conformation of individual bonds
- wide-angle XRD

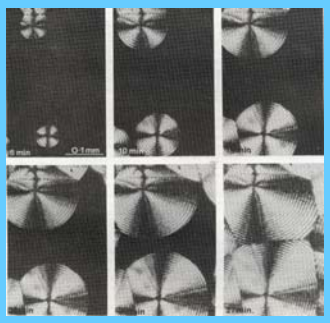
scale of crystal thickness
- 100-500 Å (10 - 50 nm)
- electron microscopy, small-angle XRD

scale of crystal aggregates
- μm scale
- optical microscopy

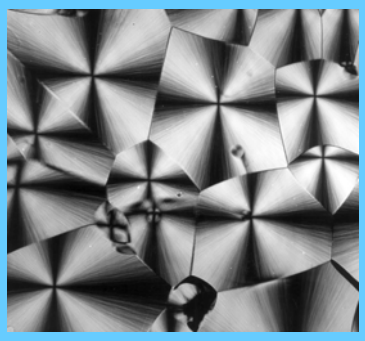
Spherulites

Isothermal crystallization of thin (5 μm) film of i-PP under polarizing microscope

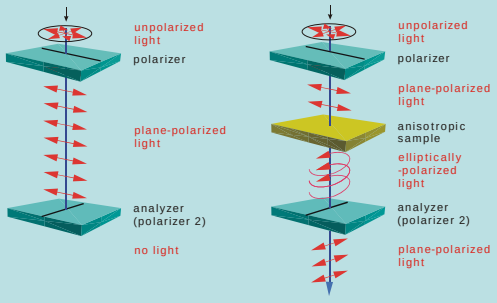
- In thin film: discs
- In bulk polymer: spheres
- Nucleate on impurities
- Grow radially at constant rate if temperature constant



Spherulites of poly(vinylidene fluoride)



Polarized microscopy

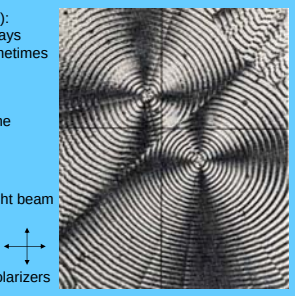


Ringed (banded) spherulites

Two types of extinction (dark areas):
- Maltese cross - always
- concentric rings (bands) - sometimes

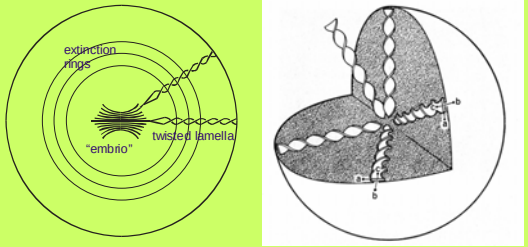
Maltese cross:
where chains are parallel to one of the polarizers

Concentric rings:
where chains are parallel to light beam



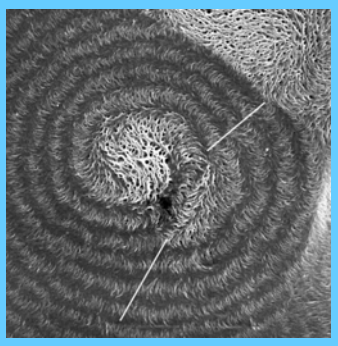
polarizers

Spherulite (schematic)



A twisted lamellar polyethylene crystal grown from concentrated solution (TEM)

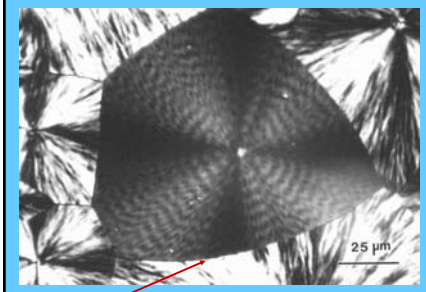
SEM of polyethylene spherulite



$HMnO_4$ etched surface

Lines show boundary between right/left lamellar twist

Spherulites of two different crystal forms can coexist – proof that form determined at nucleation



Spherulites of Form II (light) and Form III (dark and ringed) of Isotactic Poly(1-Butene).

Lotz B, Thierry A Macromolecules 2003;36:286

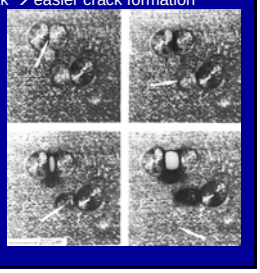
Lotz B, Cheng SZD Polymer

Note curved spherulite boundaries – Which spherulite grew faster?

Properties of spherulites

- small supercooling → few nuclei → **large spherulites** (up to 1 mm)
- large supercooling → many nuclei → **small spherulites** (down to 1 μm)
  (Nucleation rate increases more steeply than growth rate with increasing ΔT)
- **impurities** and low m.w. fraction accumulate at growth front
  – → spherulite boundary planes are weak → easier crack formation and propagation
- **small spherulites** in quenched polymer
- – **better mechanical properties**

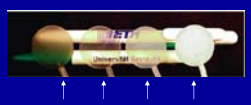
stretching



(from Frederich & Defor, 1975)

Properties of spherulites

- **nucleating agents** – additives to increase nucleation rate, reduce spherulite size
  (routinely used in PP)
- **transparency:**
  – large spherulites, high crystallinity → opaque
  – small spherulites or no spherulites,
  → transparent



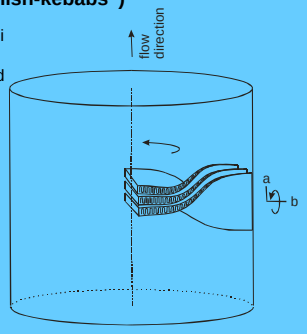
i-PP containing: 0.1 0.5 2 10
wt% DMBDS nucleating agent

(from Kristiansen & Smith, 2003)

- Where are spherulites found?
  - in polymers crystallized from **static** (quiescent) **melt**
- Which processes lead to spherulitic morphology?
  - compression moulding, injection moulding

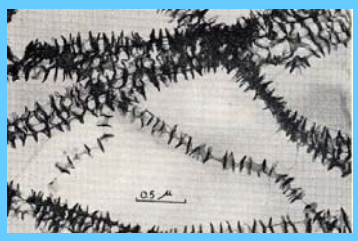
Cylindrites or row-nucleated structure ("shish-kebabs")

In flowing melt – rows of nuclei
- nuclei densely spaced
→ lamellae grow radially in 2-d



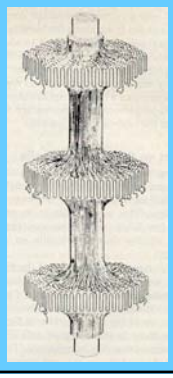
- Where are cylindrites found?
  - in polymers crystallized from **flowing melt**
- Which processes lead to cylindrite morphology?
  - melt-spinning of fibres, film blowing

Crystals from stirred solution



Transmission electron micrograph of polyethylene "shish-kebabs"

Shish-kebabs



- extended-chain central fibre - forms first
- folded-chain lamellae grow epitaxially

- In flowing solution or melt chains partially aligned
- → entropy of melt (solution) is lower

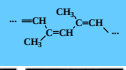
→ S_f-S_c = ΔS_f smaller

→ $T_m = \Delta H_f/\Delta S_f$ higher

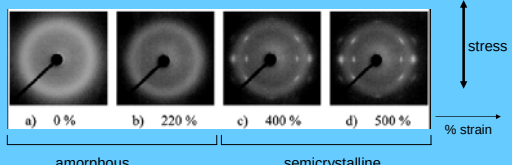
→ aligned molecules are more highly supercooled
→ nucleate first

Stress-induced crystallization

Entropy of melt S_l is reduced even more in stretched rubber
Natural rubber - T_m not far below room temperature
→ T_m raised above r.t. on stretching
- stress-induced crystallization (reversible)
→ high toughness (self-reinforcing)



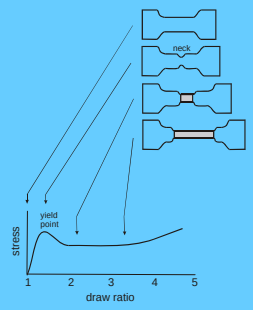
poly(*cis*-isoprene)



X-ray diffraction

Murakami et al, 2002

DEFORMATION MECHANISM OF SEMICRYSTALLINE POLYMERS



DEFORMATION MECHANISM OF SEMICRYSTALLINE POLYMERS