

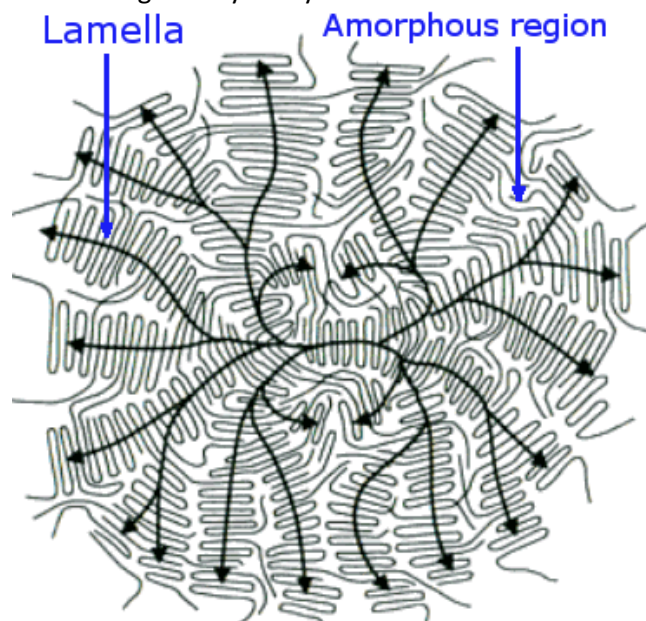
## Polymers Lab- *Hot-Stage Optical Microscopy*

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**Objectives** Observe the crystallization and recrystallization of a polymer (polypropylene) during heating and cooling

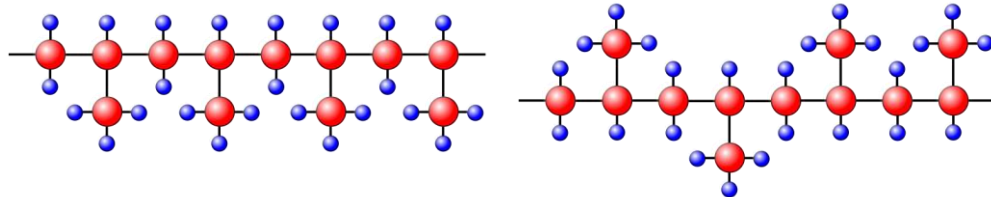
**Background** Polymer crystallization occurs if it is energetically more favorable for polymer chains to be oriented with respect to one another than to be randomly oriented as they are in amorphous bulk polymers. Remember Gibbs free energy,  $\Delta G = \Delta H - T\Delta S$ . The enthalpy term comes from the energetic interactions between adjacent strands, which usually consist of hydrogen bonding and van der Waals interactions. Because polymer chains consist of thousands of monomer units, the total energy of these interactions may be quite large. Simultaneously, however, because polymer chains' large size and interconnectedness via covalent bonds, entropic forces can also be quite large in polymer chains. The entropic term increases proportionally to temperature, driving chain motion. Chain motion allows chains to get into proximity in order to form a crystal, but too high a temperature allows entropy to overcome enthalpy and leads to crystal melting.

How does polymer crystallization occur? It begins at a nucleation site. A nucleation site can be an inorganic additive (talc, sand, etc.) or a site of local density fluctuation where several polymer chains have moved close to one another forming a small bundle of chains, known as a fibril. From there, the crystal (a.k.a. spherulite) continues to grow outward, drawing in fibers from the amorphous bulk and folding and/ or packing them into the crystal as they interact with the neighboring ordered chains. The result is a beautiful birefringent spherical crystalline domain, which is not as ordered as the inorganic crystals you are familiar with.



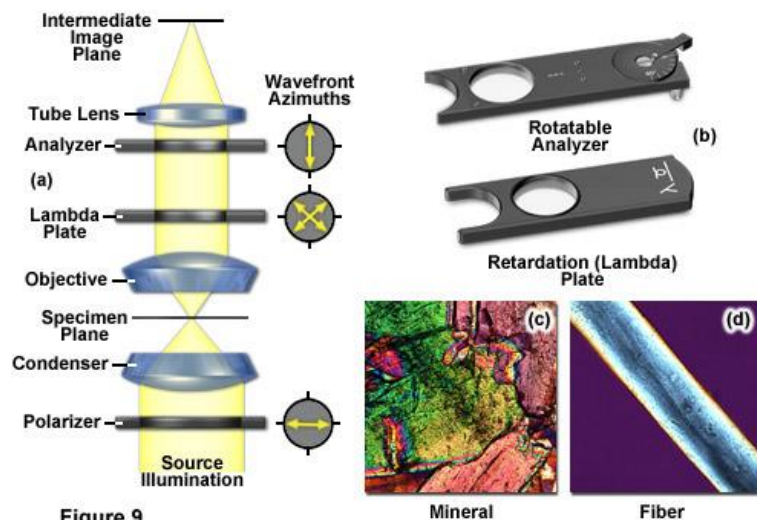
Enthalpy drives like chains to group with like. This only occurs if the enthalpy of chain-chain interactions is relatively high.

In the case of isotactic polypropylene, the strands can pack close together and bind through van der Waals interactions. In the case of atactic polypropylene, however, the enthalpy of chain-chain interactions is relatively low because of steric hindrance due to the protruding  $-CH_3$  groups, so spherulites do not readily form. Below are ball and stick 2D models of polypropylene depicting two tacticities: isotactic on the left and atactic on the right.



To measure and observe polymer crystallization, we can use optical microscopy. Spherulites consist of hundreds of thousands of polymer molecules and can grow large enough (diameter = 10 -100  $\mu\text{m}$ ) to be seen even under low power optical microscopes. To distinguish polymer crystals from amorphous regions, we use a special property of the crystals alluded to before—birefringence. We image by passing the incoming light through one polarizer and then passing the transmitted light through a polarizer that is “crossed” or polarized at a  $90^\circ$  with respect to the incoming light. From physics, we know that in air, a light beam in air that is passed through crossed polarizers will be completely canceled. This is also true in amorphous materials including inorganic and polymer glasses. Thus, any amorphous polymer regions in our sample will appear very dark. The spherulites on the other hand, rotate the incoming polarize light due to their birefringence, and that light emitting from the crystalline regions is not canceled and appears very bright against the dark background.

**Polarized Light Microscope Optical Pathways and Components**



**Figure 9**

Mineral

Fiber

- Discussion**
- Describe how a hot-stage optical microscope works and how the polarizers influence lighter or darker images.
  - Describe the process of polymer crystallization, as well as the phenomenon and fundamental science of a spherulite and birefringence.
  - Low density & electrically insulating nature of polymers make them ideal for optical microscopy why?
  - What are some applications of semicrystalline polymers? What material properties make semicrystalline polymers useful for these applications?
  - Explain results you would expect from hot-stage optical microscopy if you tested the 2 polymers from the other 2 labs.
- Materials**
- High molecular weight polypropylene (PP)
  - Low molecular weight polypropylene (PP)
- Equipment**
- Hot-stage optical microscope
- Experiment**
- Place glass slide on hot plate
  - Place bead of polypropylene on glass slide
  - Carefully heat hotplate to above the melting temperature of the polymer
  - When the bead begins to melt, carefully use a glass coverslip to smear the bead to form a thin even layer of melted polymer
  - Turn on Zeiss microscope. Place polypropylene film sample into hot-stage chamber
  - Place hot stage chamber onto microscope platform
  - Adjust the stage position and focus
  - Program the hot stage optical microscope to heat the polymer sample to 200C and cool to room temperature
- References**
1. <http://zeiss-campus.magnet.fsu.edu/articles/basics/contrast.html#polarized>