Polymer crystallization

Objective

The objective of this laboratory is for you to explore the kinetics of polymer crystal growth and melting.

Preparation

Read the introduction of the paper on thin film PEO crystallization posted at the Compass web-site.

Equipment and samples

- Polarized light optical microscope; hot-stage; video camera; computer and video capture software.
- Poly(ethylene oxide); acetonitrile solvent; spin coater.

Introduction

Crystallization from a melt is the most fundamental of all phase transformations in materials. Control and understanding of the kinetics of crystallization is crucial for controlling the microstructure and, therefore, the properties of materials. We have encountered many examples of crystallization from the melt or crystallization from solid solutions in MSE 307/308: i) the latent heat of materials used for thermal energy storage; ii) precipitation hardening; and iii) the eutectic microstructure of binary organic alloys.

In general, a crystalline phase must first nucleate. The fundamental kinetics of nucleation are often difficult to determine because the rate of heterogeneous nucleation at defects, impurities, and surfaces is much faster than the homogeneous rate of nucleation within the pure bulk liquid. After a nucleus forms, the kinetics of crystal growth determines the overall rate of the phase transformation. For growth from solid or liquid solutions, the rate limiting step in the kinetics is often mass diffusion. For crystal growth from a melt, heat transfer plays an important role for metals, ceramics, and semiconductors, but for large molecules and polymers, the microscopic kinetics associated with attaching a large molecule or polymer segment to the growing crystal are typically the most important consideration. Crystal growth of polymers is a relatively slow process and therefore more amenable to direct observation by optical microscopy.

Session 1: Measure the crystallization and melting kinetics of PEO in the thick film limit.

- Spin-coat a microscope slide with a relatively thick layer of PEO.

- Load the microscope slide into the hot-stage and raise the temperature above the melting point. Focus the microscope and then adjust the polarizers to make the image dark; i.e., use crossed-polarizers.

- Cool the stage to some temperature below the melting point to nucleate PEO crystals and then adjust the temperature to observe the growth or melting of these crystals at different temperatures. The crystals will show strong optical contrast because of birefrigence; unlike the melt, the index of refraction of spherulites is not isotropic. Measure the growth or melting rate by analyzing video images of the motion of the liquid/crystal interface.

- For elements and simple compounds, the growth and crystallization rate is often a linear function of the supercooling or superheating of the crystal, i.e., the deviation of the temperature from the equilibrium melting point. Is that the case here?

Session 2: Measure the crystallization and melting kinetics of PEO as a function of film thickness.

- Spin-coat a microscope slide with a thin layer of PEO; the TAs will provide a calibration of thickness as a function of the rotation rate of the spinner.

- Follow the same procedure as before but now explore how the kinetics change as a function of film thickness.