

Polymer crystallization

Objective

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

Preparation

Read the reference papers on thin film PEO crystallization posted on the Compass2g web-site.

Equipment and samples

- Polarized light optical microscope; hot-stage; video camera; computer and image capture software
- Poly(ethylene oxide); acetonitrile solvent; silicon wafers, spin coater.
- DSC, Al pans, crimper.

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 courses: 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.

Observe the crystallization of PEO under polarized light microscope

- Spin-coat a silicon wafer with a relatively thick layer of PEO.
- Load the coated wafer on a microscope slide and place it into the hot-stage. Focus the microscope on the specimen and be sure to add a calibrated scale bar. Raise the temperature above the melting point. Once melted, adjust the polarizers to make the image dark; i.e., use crossed-polarizers.

Measure the crystallization kinetics of PEO at a function of crystallization temperature.

- 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 birefringence; unlike

the melt, the index of refraction of spherulites is not isotropic. Measure the growth or melting rate by analyzing a series of images of the motion of the liquid/crystal interface. Make sure that the crystals do not impinge on each other or grow too far off screen when measuring the radius. Homogeneous nucleation is preferred, so try to avoid dust or scratches on the surface if possible.

- Analyze the temperature dependence of the crystal growth kinetics by repeating the experiment at several different temperatures between 30°C and 45°C. You may need to adjust the cooling rate in the Linksys software to get the best results.
- Use DSC to determine the melting temperature and the latent heat of PEO. From the kinetics analysis, find the interfacial energy for PEO crystals. Comment on what this value means; can you find a value from the literature for comparison?

DSC program:

Step 1: Hold for 1 min at 25 ° C

Step 2: Heat from 25 ° C to 100 ° C at 25 ° C/min

Step 3: Hold for 2 min at 100 ° C

Step 4: Cool from 100 ° C to 15 ° C at 20 ° C/min

Step 5: Hold for 1 min at 15 ° C

Growth Rate Equation:

$$G = G_o \exp\left(\frac{-\Delta E}{R(T - T_g + C)}\right) \exp\left(\frac{K}{T(T_m - T)}\right) \quad (1)$$

Where G_o is a pre-factor, R is the ideal gas constant, T_g is the glass transition temperature, ΔE and C are constants for viscous flow, and K is the growth constant. For PEO, ΔE is approximately 17,000 J/mol, C is around 50, and T_g is 213 K.

The growth constant can also be written in terms of several other factors:

$$K = \frac{J * b_0 * \sigma_1 * \sigma_2 * T_m}{k_B * \Delta H_f} \quad (2)$$

Where J is a constant equal to either 2 or 4 (depending on the growth regime), b_0 is the thickness of the growth layer ($\sim 4.2 \times 10^{-10}$ m), T_m is the melting temperature, ΔH_f is the latent heat of fusion, k_B is Boltmann's constant, and $\sigma_1 \sigma_2$ is the product of the interfacial energies.

More information about these equations can be found in the posted references.