Experiment 16:

Kinetics of Crystallization of Poly(ethylene oxide)

(Special iLab)

Aim: (a) To measure the rate of crystallization and relate this to polymer crystallization kinetics.

(b) to measure the rate of volume transformation and to determine the Avrami exponent of thin film crystallization.

This experiment is an "iLab", or "internet laboratory". You can perform the entire experiment remotely from any Athena Sun or Linux workstation. The experiment is available 24 hours a day during the designated period. You may access the experiment by pointing your web browser to https://polymerlab.mit.edu. The first time you use the system, you will need to register as a new user, and then allow 24 hours for confirmation from the system administrator. After you receive confirmation, you will be able to reserve a time on the system to run the experiment. Reservations are limited to a maximum of 90 minutes. Once you are familiar with it, the experiment itself should take about 90 minutes. If you need more time, you may do so by reserving the microscope more than once. When opening the Polymer Lab window, it can take several minutes for the Java applets to load. See the User Manual for further information about operating the user interface to the microscope.

Materials and Apparatus:

Poly(ethylene oxide) (MW 100,000)

polarized light microscope

hot stage

Diffused light source

Brief Background: When they crystallize, polymers form spherical structures called "spherulites" or literally "little spheres" with diameters usually in the range of 0.5-100 mm. A spherulite consists of lamellar crystals that are radially arranged to form the supra-molecular structure. Three essential attributes of spherulitic formation will be studied in this experiment.

1. Spherulite morphology of polymers can be observed by optical microscopy. Polymer chains within a spherulite interact with light to produce patterns with "birefringence" characteristics. (see Rabek, *Experimental Methods in Polymer Science*, pp443-456 and470-472,and Schultz, *Polymer Crystallization*, pp127-138 for more information).

Birefringence: An ordinary beam of light is an electromagnetic wave vibrating equally in all directions around the axis of the beam. Certain *anisotropic* (i.e. not the same in all directions) materials have the property that light waves vibrating in one direction (the "fast axis") are transmitted through the material faster than light waves vibrating in another direction perpendicular to it (the "slow axis"). This property is called optical anisotropy, or birefringence. In polymers, the origin of birefringence lies in the greater polarizability of the molecules along the chain axes than perpendicular to them. When a polymer is deformed to large strain or crystallized, the chains line up. The index of refraction is different along the chain axis than across it, resulting in a birefringent medium.

A film or grating which only permits light wave vibrating only in one direction to pass through it is called a *polarizer*. Light which passes through a polarizer is polarized in one direction, and has a single axis of vibration. If this light then encounters a second polarizer (called the *analyzer*) oriented parallel to the first, the light will pass through the

analyzer as well. If the analyzer is oriented 90 degrees to the first, then no light will pass through the second film.

Now suppose a specimen is placed between the polarizer and the analyzer. If the specimen is birefringent, the light from the polarizer will be split into two components and enter the analyzer as two waves out of phase with each other, which appears a rotation of the axis of vibration. When the axis of vibration is parallel to either polarizer or analyzer, no light will pass and the specimen will appear dark. When the axis of vibration is at 45 degrees to the plane of vibration of polarizer or analyzer, the specimen will appear brightest. The result is the well-known "maltese cross" pattern, shown in fig 26.14 of the handout from Rabek, *Experimental Methods in Polymer Science*, p454.

2. The second aspect of the experiment examines the formation of the spherulites of PEO using optical microscopy. The growth rate of the spherulites can be measured and corresponds to the growth of individual lamellae within a spherulite. This growth rate allows us to examine the mechanism of growth of individual lamellae. For a brief background on kinetic theories of polymer crystallization, see Schultz, *Polymer Crystallization*, pp 140-157.

3. The third aspect of polymer crystallization is the total volume transformation of the sample. Spherulites nucleate first either by homogeneous or heterogeneous nucleation. The number of nuclei crystallizing is usually found to increase with time for a given temperature of crystallization. The expanding nuclei then grow out radially at constant rate (usually) and fill the entire volume of the sample. A brief analysis of the volume transformation, using the Avrami equation, can be found in the supplemental reading from Schultz, *Polymer Crystallization*, pp176-182.

Procedure:

1. Place a sample of about 10-20 mg of PEO powder (approximately) on a glass slide and cover with a cover slip. Place the glass slide in the hot stage mounted on the microscope and heat to about 100 C to melt and consolidate the powder. Allow the slide to cool. *(This part has already been done for you. When you first log in, this should be at about room temperature. The polarizer is fixed in position on the microscope.)*
2. With the sample at room temperature (about 25 C), adjust the microscope settings (magnification, aperture, field stop, light exposure) to get an acceptable view of the sample. Use the autofocus button if necessary to improve the focus whenever the settings are changed. Your field of view will be limited at low magnification by the viewing port in the hot stage, resulting in a circular viewing area.
3. Rotate the analyzer in and out of position (90 deg to polarizer). When the analyzer is out of position (i.e. parallel to polarizer), this is call "bright field". When the analyzer is in position, it passes polarized light perpendicular to that passed by the polarizer. Record what you observe.
4. With the analyzer in position, instruct the hot stage to raise the sample temperature to about 80 C at about 10 deg/min and hold it there for about 5 min, to completely melt the sample (Question: how will you know it has melted?). Whenever you are heating or cooling the sample, remember to turn on the video stream option so that you can observe the changes in the sample. The video capture rate is about 2 frames per second. (Most other operations with the microscope will automatically cause the camera to capture a new image.)
5. After the sample has completely melted, instruct the hot stage to cool the sample to the first desired crystallization temperature, T_c=55 °C. The cooling should be performed as rapidly as possible. If the hot stage has been equipped with a supply of liquid nitrogen, this can be done as fast as 10 deg/min. If not, you must rely on the hot stage to lose its

heat to the ambient air. In this case, estimate the cooling rate from the observed temperature readings.

6. Make a note of the temperature at which you first begin to observe spherulites form in the sample. Observe whether these spherulites nucleated in your field of view, or did they nucleate outside your field of view (possible if the sample size is larger than the field of view at the magnification used) and grow into your field of view.
7. Re-heat the sample slowly (e.g. 2 C/min) to 80 C and note the temperature at which the spherulites melt. This is T_m.
8. Repeat this procedure, this time recording the images as they are collected by the microscope, for later analysis. Be sure to start recording a little before you expect the first nuclei to appear, and stop recording as soon as all the spherulites are impinged. The recorder can be started and stopped using the "recorder" pulldown at the top of the window.
9. Repeat steps 5 through 8 for each of the following crystallization temperatures:

$$T_c = 52.5\ °C,\ 55\ °C,\ 57.5\ °C \text{ and } 60\ °C$$

When all the data has been recorded, you should log out of the microscope, so that others may use it. You can analyze your recorded data immediately or at a later time by logging back in to the server and retrieving the corresponding "experiment". Each image in a recorded session is stored with information about the magnification, time of collection, and temperature of the sample. The "view slideshow" option creates a *.smil* video file which can be viewed using Quicktime. Selected images from the video stream may be analyzed using the ImageJ software provided on the polymerlab server, or any other method of your choice. The "analyze image" option opens up an ImageJ window so you can extract information about the size of the spherulite at different times. (Hint: the Process/binary/threshold and Process/binary/outline options in ImageJ are useful to

simplify the image to black and white pixels; the "draw square" tools is useful to inscribe a spherulite, whereupon you can read off the size of the square in pixels from the ImageJ control panel. If the spherulite nucleates outside of your field of view, you will not be able to inscribe the entire spherulite, but you can still use the tools to estimate the a relative diameter or the relative location of the growth front, since it is only the rate of change of this location that really matters for the analysis to follow.) To convert number of pixels to length, use an image where you can measure the diameter of the viewport on the hotstage; this viewport is 1.38 mm in diameter. Using your data regarding spherulite size versus time at each temperature, perform the analyses indicated below.

Analysis:

1. For the four crystallization temperatures used, plot T_m vs T_c and extrapolate to the $T_m=T_c$ line to determine the *equilibrium* melting temperature, T_m^0.
2. Plot $\ln v + U^* / R(T - T_\infty)$ vs $1/T\Delta T$ to obtain an estimate of the mean surface energy $(\sigma\sigma_e)^{1/2}$ of the crystal lamella. For PEO, you can assume the following parameters:

   T_∞=176 K U^*=29.3 kJ/mole Δh_f=2.43x10^9 ergs/cm^3

3. Estimate the fraction crystallized, χ, from the area of the spherulites divided by the total viewing area and plot ln(1-χ) vs time, t. From this, determine the Avrami exponent, m.

Discussion:

1. How does your estimate of the *equilibrium* melting temperature, T_m^0 compare to the literature value of 343 K?

2. How does the observed growth rate vary with crystallization temperature? Do the observed growth rates confirm the assumed kinetic model? Is there a temperature at which you expect this growth rate to go to zero? Explain.

3. How does the number of nuclei change with time and with crystallization temperature, Tc? Is there a temperature at which you expect the rate of formation of nuclei to go to zero? Explain.

4. Interpret the value obtained for the Avrami exponent in terms of the actual geometry of the crystallization experiment performed here (i.e. a thin film of molten polymer crystallizing to form a thin solid film).