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Atomic Force Microscopy of Poly(ethylane-oxide) Crystalization

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Atomic Force Microscopy of Poly(ethylene-oxide) Crystallization

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April 26, 2016

Abstract

Polymer crystallization is a complex process which is influenced by a variety of factors. Atomic force microscopy is used to explore the material properties of polymer crystals. Poly(ethylene-oxide) is used in a variety of molecular weights as the sample. In addition, a variety of sample preparation methods and microscopy modes were tested. A relatively new imaging technique was identified for the characterization of polymer crystals: amplitude modulation-frequency modulation viscoelastic mapping. This mode was used to measure material properties such as stiffness and dissipation.

Dedication

To Maman and Papa.

Honor Code Declaration

I affirm that I have carried out all my academic endeavors with full academic honesty.

Acknowledgements

Contents

Chapter 1

Background

1.1 Polymer Crystallization

The process whereby molecules form crystalline structures is complex and difficult to study using real-time spectroscopy techniques. It is driven by three primary processes: diffusion field, interface kinetics, and capillarity. Diffusion field is the transportation of unbound molecules to the growth front of the crystal. Interface kinetics describe how these molecules bind to the surface. Capillarity is the surface tension which minimizes interfacial energy. These three processes are sufficient to describe crystal growth. Crystallization occurring with smaller constituent molecules progresses more rapidly and is thus difficult to characterize [1].

Polymer crystals grow more slowly due to viscosity of the liquid. In addition, polymers consist of longs chains of monomers which cannot attach individually to the crystal growth front. As they must bind at the crystal front in a limited number of adjacent sites the polymer chains would need to fully extend to perfectly crystallize. The crystallization rate however is typically too fast for this optimal arrangement which results in a lamellar crystal with amorphous chain folds at the surface. This contrast between small molecule and polymer crystallization can be seen in figure 1.1. The lamellae of polymer crystals are typically quite wide yet very thin. Thus polymer crystal are defined as semi-two-dimensional [1].

It takes a substantial amount of time to grow polymer crystals. There is an exponential increase in time proportional to the length of the constituent polymer chains. Cooling time limits impose chain folding and hence, less perfection in the crystal structure. The degree of chain folding increases lamellar thickness which subsequently changes the melting point of the crystal [1].
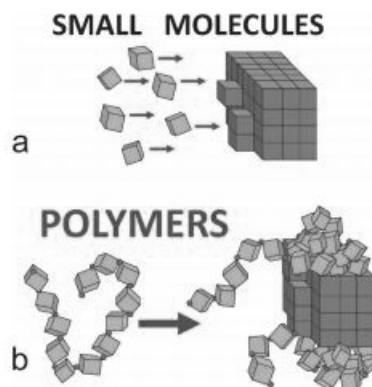
7

Figure 1.1: Schematic representation of the difference between the crystallization of polymers versus small molecules. (a) Small molecules arrive randomly at the growth front and are generally uninhibited in their attachment and reorganization on the surface. (b) Polymers are not discrete units but rather chains of unit segments. This severely limits their ability to attach to the growth front, resulting in chain folding and the formation of lamellar crystals having amorphous surfaces. (Courtesy of Günter Reiter) [1].

The actual process of polymer crystallization occurs first with the formation of a nucleus of critical size. This can arrive independently in the melt from happenstance polymer orderings. Once a nucleus has formed the growth front must propagate and lead to the bulk crystal. As described previously, many factors influence this process [2].

In particular, Poly(ethylene oxide), also known as poly(ethylene glycol) depending upon its molecular weight, is used in a variety of applications ranging from industry to medicine. Its crystallization has been widely studied as it is both non-toxic as well as easy to work with. The molecular structure can be seen in figure 1.2.
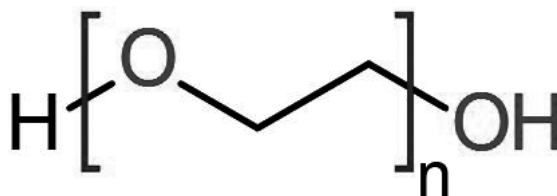

Figure 1.2: Molecular diagram of poly(ethylene-oxide).

We work primarily with PEO of molecular weight 4000 but exploring other weights may reveal interesting features of crystallization which are dependent upon polymer chain length.

1.2   Atomic Force Microscopy

1.2.1   Instruments and Basic Operation

The basic instrumentation of the atomic force microscope (AFM) is quite simple given the power of the device. The device itself can be seen in figure 1.3.
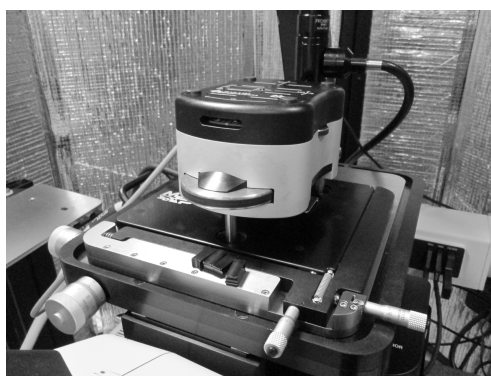
Figure 1.3: Asylum Research MFP-3D Atomic Force Microscope

A sample is mounted on the stage which can be shifted with piezoelectrics. The tip, on the end of the cantilever, is brought close to the surface, also with piezoelectrics. This surface-tip distance can be controlled down to the angstrom. The AFM feedback mechanism is incredibly precise. A laser is reflected off the tip and hits a photodetector which is fundamental to the feedback procedure. Any flexure in the tip will cause the laser point to shift on the photodetector. Depending on the mode of operation, this initiates a feedback that adjusts the position of the cantilever using piezoelectrics. This can be seen schematically in figure 1.4. A wide variety of modes can be used with the AFM, each of which have different advantages depending on the sample [4].

The particular AFM in use at Union College is Asylum Research MFP-3D. It is mounted with an inverted optical microscope for bio-AFM. The entire unit is seated on an isolation table and closed in an isolation hood during imaging. The entire setup can be seen in figure 1.5.

Figure 1.4: Schematic representation of the components of an atomic force microscope. (Courtesy of the University of Massachusetts, Amherst).
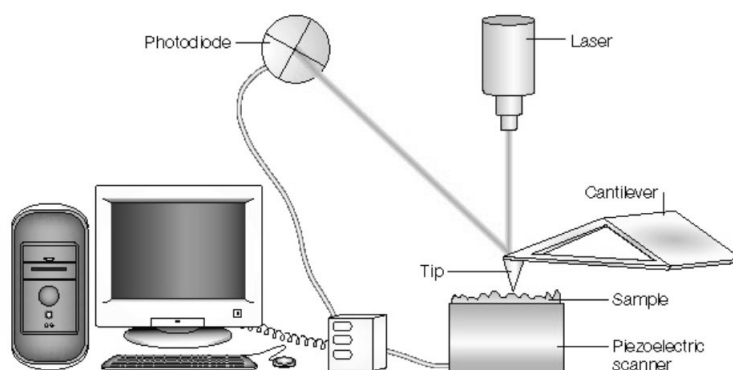
1.2.2   Contact Mode

Exactly as the name implies, contact mode involves direct contact between the tip and the sample surface. A set point is set to limit how much deflection is acceptable in the cantilever before retracting from the surface. As the tip scans across the surface, it maintains the same deflection constantly by extending or retracting with piezoelectrics. The disadvantage of this method is that both the tip and surface can be easily damaged. Too much force applied to the surface will result in damage to the sample and the tip. In addition, this mode is very difficult to use with soft samples like cells or soft polymers because they are more sensitive to direct contact and can easily deform or be damaged [4].

1.2.3   Amplitude Modulation (AM) Mode

Amplitude modulation (AM) mode is a non-contact method of imaging the sample. It is also referred to as tapping mode. In this mode, the cantilever is oscillated at a set frequency. The frequency of the tip, as recorded from the photodetector, is monitored. When oscillating at resonant frequency in free air, there is a phase shift between the oscillations of the cantilever and tip of roughly ninety degrees. However, when the tip approaches within a few angstroms of the surface, there is an attractive region which influences the oscillation of the tip. The feedback is such that the amplitude will modulate to maintain the frequency of oscillation. In addition, as in contact mode, there is a set point, used to ensure the tip does not oscillate into a structure on the sample [4].
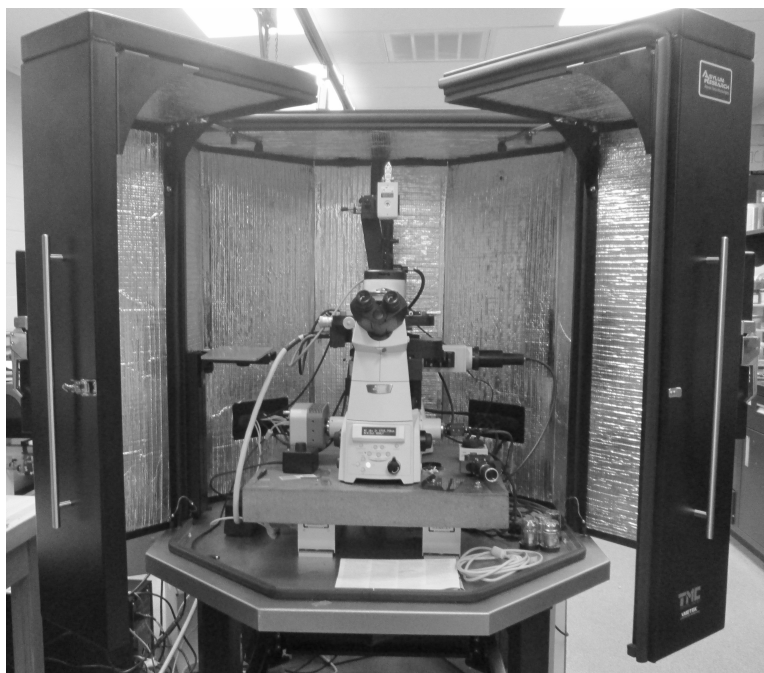
Figure 1.5: Asylum Research MFP-3D AFM at Union College.

1.2.4 Fast Scan AFM

In each topographical mode of the AFM the user can adjust the scan rate. Typically, we operate between 0.25 Hz and 1.00 Hz. The crystallization rate of PEO is quite rapid however, so to observe the growth front we need to operate with a much faster scan rate. In an attempt to accelerate the imaging process, we have increased the scan rate up to 9.77 Hz however image quality degraded significantly at higher than 4.88 Hz. Stiffer tips may allow us to operate at a faster rate without as much degradation in the image.

1.2.5 Force Spectroscopy

This mode entirely eliminates the lateral scanning motion of the tip. It is used to acquire force data at a single point on the sample surface. The tip is simply extended into the sample until the deflection set point is reached. The tip is then retracted and the result is a force curve as shown in figure 1.6. By analyzing the contact region of the curve, the material properties of the sample can be determined. However, due to the size of the tip, only the surface properties are being measured [4].

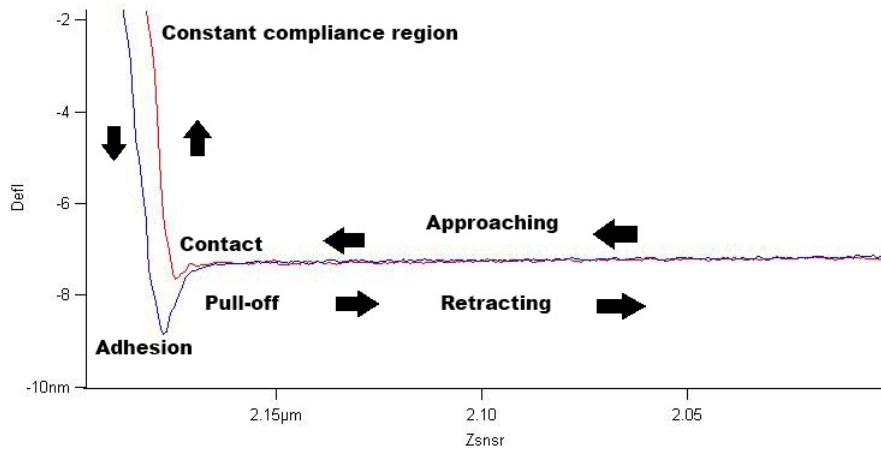Figure 1.6: Force curve acquired with the atomic force microscope. The red line represents the approach of the tip while the blue represents the retraction. The contact point is clearly labeled for the red line and shows the region of interest for acquiring material properties.

1.2.6 Imaging Liquids

Imaging liquids with the AFM is very challenging as there is a strong tendency toward capillary wetting between the liquid sample and the tip. If the tip become submerged at all in the polymer melt, it becomes inoperable, so great care is taken to use a very gently approach. Liquid imaging is done in AM mode oscillating in the repulsive regime to avoid bridging of the polymer melt. Unfortunately, as crystallization progresses the surface descends which makes it very challenging to maintain contact for imaging of the actual crystallization process.

1.2.7 Amplitude Modulation-Frequency Modulation (AM-FM) Viscoelastic Mapping Mode

This mode operates by summing two excitation signals and sending them to the cantilever simultaneously. They excite two vibrational modes; usually the first and second resonant frequencies of the tip [5]. This requires a special high frequency cantilever holder which can be seen in figure 1.7. A schematic of the actual AM-FM operation is shown in figure 1.8.

The first operates in amplitude modulation mode as was described previously. The amplitude and phase are monitored at a fixed frequency to determine the loss tangent. The loss tangent, $\tan \delta$, is the response of a material to cyclic excitation. It is defined as the ratio of dissipated energy to stored energy. "The angle
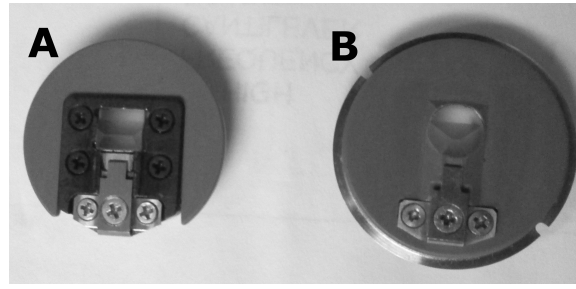
Figure 1.7: (A) high-frequency cantilever holder, (B) standard cantilever holder.

δdescribes the phase lag between an applied strain and the resulting stress in a material with time-dependent response," [5]. The amplitude is also used as the feedback to extend or retract the tip on the surface. The second resonance mode measures the phase and amplitude while adjusting the drive voltage to keep the amplitude constant. The drive frequency is adjusted to maintain the phase at 90°. The output drive voltage is used to determine viscous or dissipative forces. The output resonance frequency is used to determine the elastic tip-sample interaction. Quantitative elastic modulus and stiffness can also be determined by setting the tip geometry in the model parameters. The loss modulus is determined through the combination of storage modulus and loss tangent and contact stiffness is determined with the cantilever spring constant [5]. This is technique is very versatile and provides lots of data on the sample.
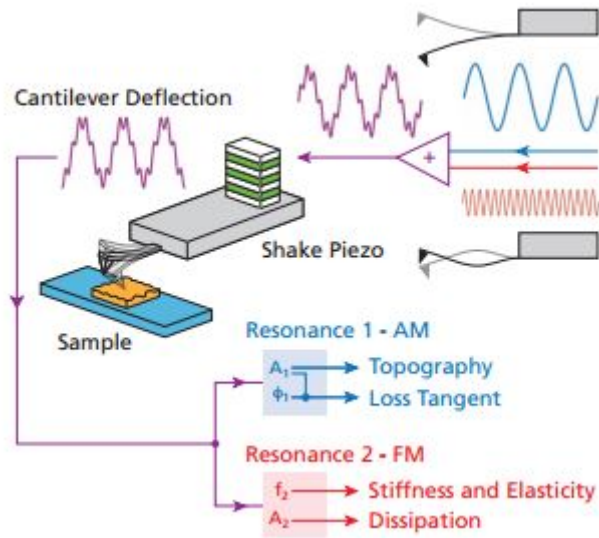
Figure 1.8: "In AM-FM Mode, two separate excitation signals (blue and red curves on right) are combined to excite two cantilever resonances simultaneously (purple curve, center). The resulting cantilever deflection (purple curve, left) is analyzed to determine the response at each resonance. Resonance 1 operates in AM mode (blue box). The amplitude A1 controls the vertical feedback loop for standard tapping mode topography, while A1 and the phase φ1 give values for loss tangent. Resonance 2 operates in FM mode (red box). Changes in resonance frequency determine stiffness and elasticity, while changes in the amplitude A2 give viscous or dissipation information," (Courtesy of Oxford Instruments Asylum Research, Inc.) [5].

Chapter 2

Experimental Procedure

2.1   Sample Preparation

Traditionally AFM samples are mounted on a glass slide and held to the stage with magnets. However, when working with the temperature control stage the sample must be quite small. In addition, since we melt the sample in some experiments, it has to be contained and not leak into the stage. However, the AFM system has only a short range in the z-axis with which to move the tip. This means the sample holder must not have a significant lip or the tip will not reach the sample at all. We experimented with unsealed differential scanning calorimeter (DSC) sample pans. Two different models were tested but both of which proved to be too deep. Using the lid of a DSC sample pan contained the sample without impeding the extension of the tip but is difficult to manipulate and does not maintain even contact with the heating element in the temperature control stage of the AFM. These initial prototypes can be seen in figure 2.1.
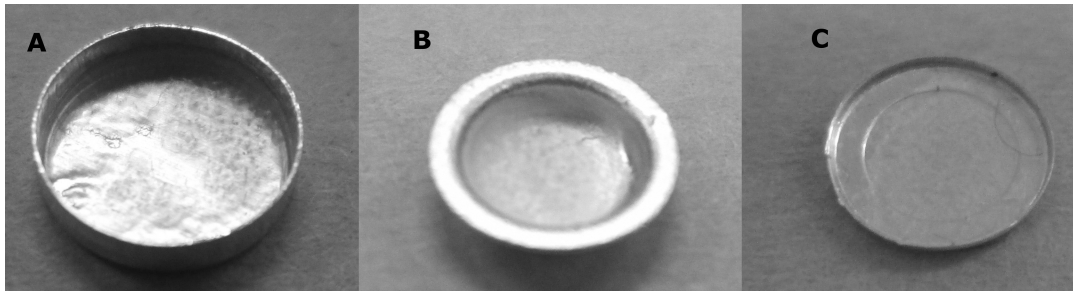

Figure 2.1: (A) and (B) DSC sample pans used to contain PEO samples. (C) Lid of a DSC sample pan.

Finally we resorted to glass coverslips with no lip. The PEO was contained in the center due to its high viscosity. Several different methods of sample preparation were tested with glass cover slips. First mechanical smoothing using a razor blade was used to smooth the surface but this process was too rough and had a risk of introducing external nucleating agents which are undesirable. We then designed and machined a rudimentary spin coater machined which operated with a household power drill. It included a heater to maintain the PEO in a liquid state. The PEO proved to be too viscous for the low RPM of the drill. Simply spreading the granular PEO across the surface and annealing on a hotplate was sufficient to produce samples for most imaging methods in the AFM. A representative sample produced using this method can be seen in figure 2.2. While this is a rudimentary sample preparation method, it limits the introduction of outside nucleating agents.
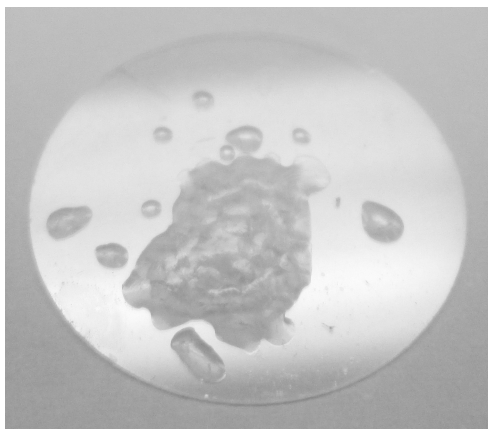
Figure 2.2: Circular glass cover slip containing unsmoothed PEO sample.

AM-FM imaging requires extremely flat samples with as little topographical variation as possible. To this end, PEO was dissolved in isopropanol (70%), deposited on a glass coverslip with a pipette, and the solvent was allowed to evaporate, leaving a thin layer of PEO. The coverslip was then adhered to a steel puck using silver paint for mounting in the temperature control stage which is magnetic. An image of the final sample can be seen in figure 2.3.

2.2 Heating Cooling Stage

Temperature control is vital to study polymers as they undergo melting and crystallization. We utilized the CoolerHeater accessory for the MFP-3D$^{\text{TM}}$ by Asylum Research. The actual stage can be seen in figure 2.4 and a schematic can be seen in figure 2.5.
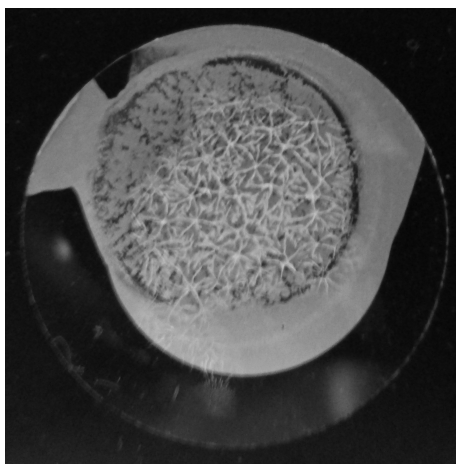
Figure 2.3: Circular glass coverslip containing thin layer of PEO and adhered to a steel puck with silver paint. Note the crystal structure visible to human eye.

Figure 2.4: Asylum Research CoolerHeater accessory for the MFP-3D$^{\mathrm{TM}}$.

By using a Peltier device, it is capable of heating to 120 °C and cooling down to -50 °C [6]. We modified our standard cantilever holder to operate at high temperatures and carried out several imaging runs which involved slowly melting and then crystallization of our sample in the AFM itself. For high-frequency imaging, the cantilever holder cannot be modified which limits the upper temperature limit to 45 °C. The heating and cooling stage introduces some noise, especially when operating near room temperature as it is constantly oscillating between a heating and cooling response. In addition, when working at low temperature, condensation tends to form on the samples which makes imaging impossible. For the purposes of our study, we are not particularly interested in very low temperatures so this did not prove to be a substantial obstacle. When operating near the limits of the stage, the Peltier device must be cooled using a coolant pump which introduces
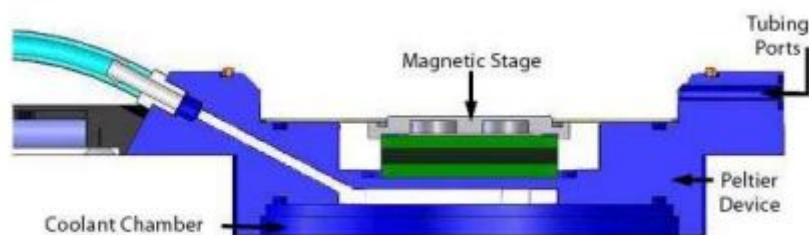
Figure 2.5: Schematic of Asylum Research CoolerHeater accessory for the MFP-3D$^{\text{TM}}$. The Peltier device sits beneath sample. Coolant flows beneath the Peltier device. There is a magnetic stage at the center to hold the sample during imaging (Courtesy of Oxford Instruments Asylum Research, Inc.) [6].

substantial noise [6]. This was unnecessary for our work. The entire control system for the heating and cooling stage, which can be seen in figure 2.6, was present during the water leak, so we performed several temperature tests to ensure the system is operating correctly.
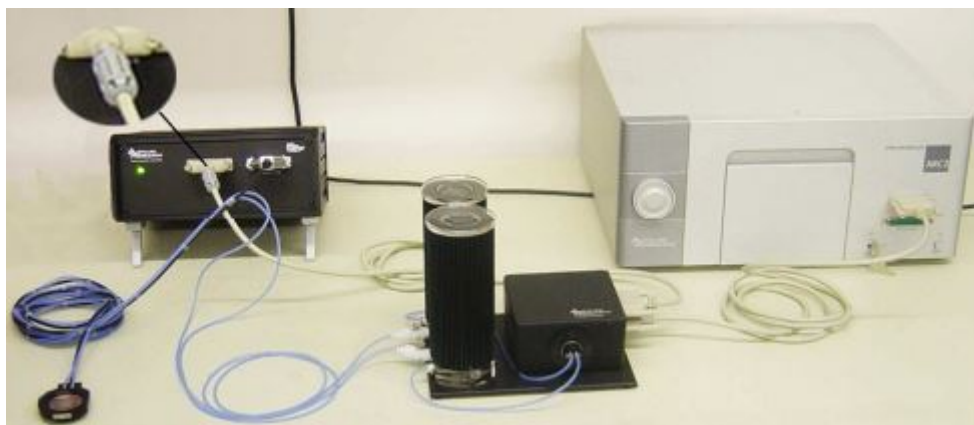
Figure 2.6: Asylum Research CoolerHeater accessory for the MFP-3D$^{\text{TM}}$, Environmental Controller, Coolant Pump and primary controller (Courtesy of Oxford Instruments Asylum Research, Inc.) [6].

2.3 AFM Probe

The probe of choice for all imaging modes used, including AM-FM, is the Olympus AC160TS-R3. It is a silicon probe with an aluminum reflex coating and designed for amplitude modulation imaging in air. The tip geometry itself can be

seen in figures 2.7 and 2.8. It is a three-sided tip with radius of 9 (7-11) nm. It has spring constant of 26 (11 – 54) N/m and a frequency of 300 (200 – 400) kHz [7]. The Olympus AC240TS-R3 probes are available as an alternative but they proved unnecessary. They have a much lower spring constant (2 N/m) for working with softer samples.
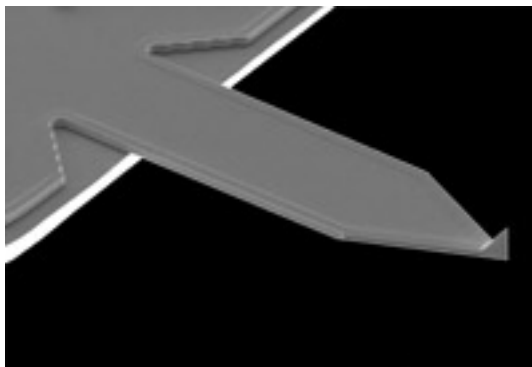
Figure 2.7: Olympus AC160TS-R3 probe, viewed from the bottom (Courtesy of Oxford Instruments Asylum Research, Inc.) [7].
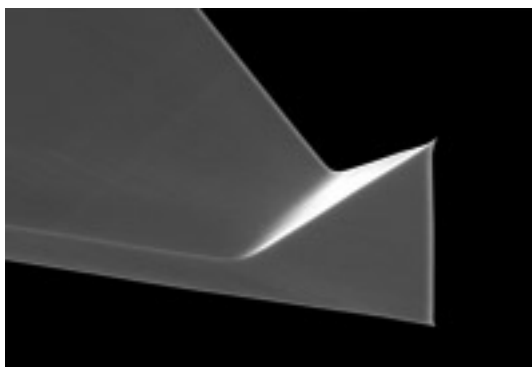
Figure 2.8: Magnified image of the tip of Olympus AC160TS-R3 probe, viewed from the bottom (Courtesy of Oxford Instruments Asylum Research, Inc.) [7].

2.4 Calibration

To work with AMFM, the system must be calibrated. If Young's modulus is desired, a sample of known modulus must be scanned prior to working with the desired sample [5]. While this would be ideal for the study of polymer crystallization, our AFM system is unable to calibrate for Young's modulus. As a result,

we instead calibrate the system to determine sample stiffness which is depended upon the geometry of the sample. The calibration for this method is fairly simple however. A glass slide is used as the clean and infinitely hard calibration sample. The tip is engaged with the sample in contact mode. We perform an indentation test to produce a force curve. The force curve will have some virtual deflection which is "a mechanical coupling of the deflection signal with the Z movement, a result of the mechanical path not being quite perfect, resulting in a slight slope in the force curve," [8]. While the error is quite small is can influence the accuracy of force measurements. This deflection is corrected for and a second indentation test is performed. The new curve which can be seen in figure 2.9 has a level approach as desired [8].
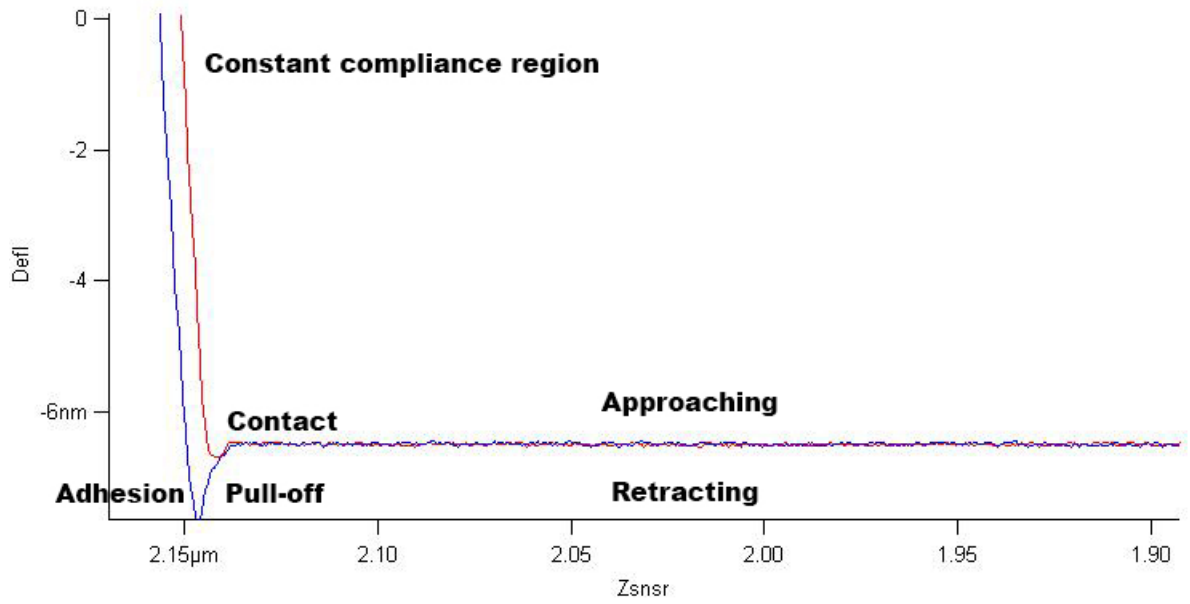
Figure 2.9: Characteristic force curve, corrected for the virtual deflection.

The second step is to measure the slope of the contact region. This slope is the inverse optical lever sensitivity (InvOLS) and is used to calculate the spring constant. Figure 2.10 gives a qualitative description of the InvOLS. This process can be repeated several times at the same location to average the value of the inverse optical lever sensitivity [8].

Finally, the AFM head is retracted to eliminate any long-range interactions. A series of frequency sweeps are performed and averaged to determine the resonant frequency of the cantilever. This is portrayed in a power spectrum plot as can be
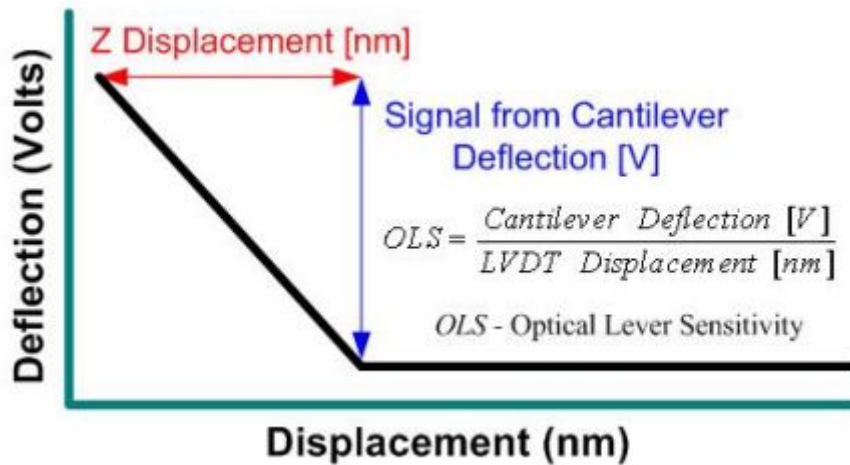
Figure 2.10: Qualitative description of the inverse optical lever sensitivity (Courtesy of Oxford Instruments Asylum Research, Inc.) [8].

seen in figure 2.11. The resonant peak is fitted. This is called the thermal fit. The software determines the spring constant using the equi-partition method [8].
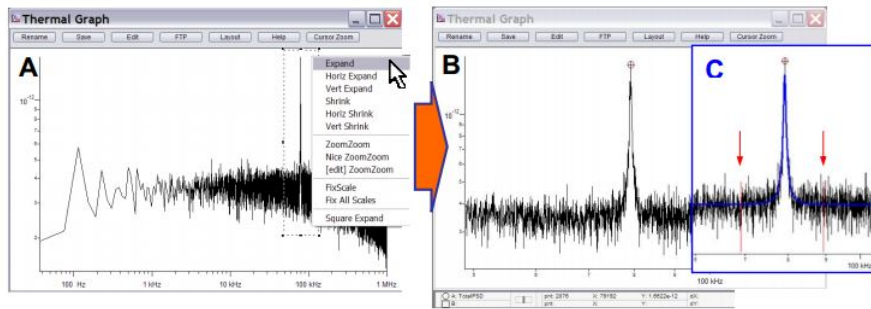
Figure 2.11: Characteristic power spectrum with (A) full plot, (B) resonant peak and (C) fitted resonant peak (Courtesy of Oxford Instruments Asylum Research, Inc.) [8].

The entire experimental protocol for calibration is detailed in appendix A.

2.5 Imaging

2.5.1 Force Curves

The acquisition of force curves is not a true imaging method but still worthy of discussion. It is the method of choice historically to acquire modulus of elasticity of samples. First use the previously described method of calibrating the cantilever spring constant with an infinitely hard sample. Then simply switch to the sample of interest and perform another indentation test. The spring constant of the cantilever on the sample can be determined using equation 2.1:

$$k_{unknown} = k_{std} \left(\frac{InvOLS_{std}}{InvOLS_{unknown}} - 1 \right) \qquad (2.1)$$

The unknown invOLS is determined for the force curve with the desired sample. The standard invOLS and k are determined from the previously described calibration method. Uncertainties in this method can be as high as 20%. In addition, this method tests only a single point on the sample surface [8]. For the purposes of characterizing polymer crystals which have ordered and amorphous regions, we would like to characterize a larger region. As such, this method was not utilized with PEO samples. The entire experimental protocol for acquiring force curves is detailed in appendix B.

2.5.2 Contact Mode

Contact mode is a very easy to use. It does not require calibration like the other imaging modes. Simply load the tip and initialize the system. The free air deflection is set slightly negatively so that the cantilever is roughly level when it engages with the sample. The set point can be chosen depending upon the nature of the sample. Soft samples should use a high set point for a gentle scan. The risk of contact mode is that the tip will have too strong of an interaction with the sample. This can result in damage to the sample or tip. With PEO, great care must be taken to engage and scan the sample gently. The entire experimental protocol for scanning in contact mode is detailed in appendix C.

2.5.3 Amplitude Modulation (AM) Mode

Amplitude modulation mode is only moderately more difficult than contact mode. It only requires the thermal fitting portion of calibration as is does not provide any data on sample stiffness or modulus of elasticity. A moderate-high set point is selected and the tip is engaged with the sample. The set point is then

lowered until a phase shift in oscillation is noted. This ensures the tip is oscillated between attractive and repulsive regimes as it moves across the sample. The set point can be further adjusted during imaging to optimize the result. The entire protocol for scanning in amplitude modulation mode is detailed in appendix D.

2.5.4 Amplitude Modulation-Frequency Modulation (AM-FM) Mode

Before beginning, the cantilever must be calibrated using the previously described method. The scan angle is changed to 90°for lateral scanning. The first and second frequencies must be tuned using the system. The first and second phases are then centered at 90°. Finally, the laser is moved to maximize the second amplitude which is quite weak. The tip is then engaged with the sample and the set point is adjusted to keep the tip in repulsive mode. Image quality is further improved by adjusting signal gains. In practice it takes about two hours to calibrate and successfully image PEO at the first temperature. The acquisition of subsequent images is much faster. The entire protocol for scanning in amplitude modulation-frequency modulation mode is detailed in appendix E.

Chapter 3

Results

3.1 Contact Mode

Using a careful approach, good resolution is easily achieved using contact mode. This can be seen in figure 3.1. However, since PEO is not a particularly rigid sample, a non-contact AFM mode is more favorable. In addition, this mode offers little more than sample topography.

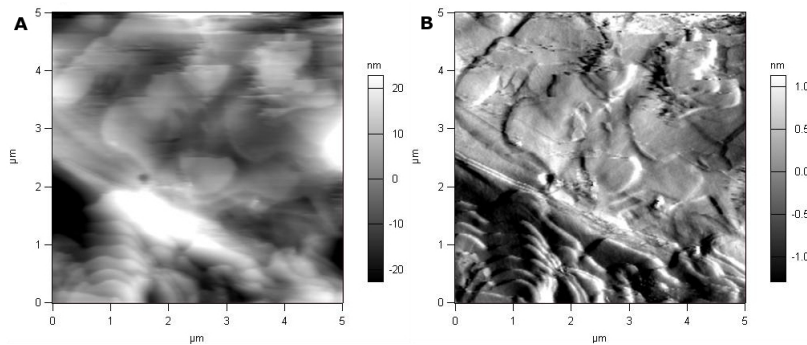Figure 3.1: /150625/IMG0022 - Contact mode image of PEO (MW 1x10^6). (A) height-retrace and (B) deflection-retrace.

3.2 Amplitude Modulation Mode

Amplitude modulation AFM is an excellent tool for characterizing PEO. As a non-contact mode, working with soft polymers is much easier and one can still acquire valuable information about the structure of the sample. An example of this is shown in figure 3.2.
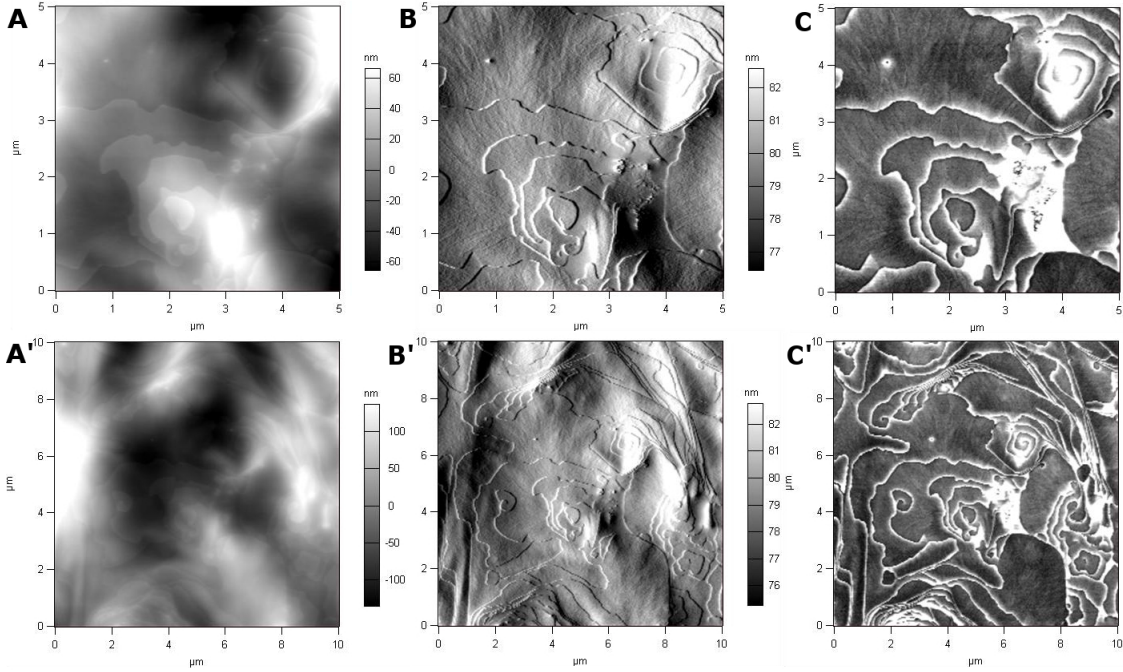
Figure 3.2: /150629/IMG0001 and IMG0003 - Amplitude modulation mode image of PEO (MW 4000). (A),(A') 5 µm and 10 µm height-retrace images respectively. (B),(B') 5 µm and 10 µm amplitude-retrace images respectively. (C),(C') 5 µm and 10 µm phase-retrace images respectively.

Using a standard cantilever holder modified for high-temperature, the sample can be imaged as the temperature approaches the melting point. Of course, once the sample melts, capillary bridging destroys the tip. In addition, at each subsequent scan there is some drift in the starting location of the tip which makes it hard to compare the sample at differing temperatures. This can be seen in figure 3.3.

3.3   Liquid AFM

In an attempt to overcome the problem of capillary bridging described previously we started with a melted sample and engaged with the liquid surface. We then took rapid images as we decreased the temperature. As can be seen in figures 3.4 and 3.5, we were able to resolve the surface of the liquid. The waves are a result of the piezo used to move the sample back and forth laterally. At the crystallization temperature the height of sample decreased significantly and the tip lost engagement. Several rapid adjustments were made to continue imaging.

While some evolution can be seen in the crystal structure, our AFM model cannot operate at scan rates high enough to characterize the crystal growth front with relevant time resolution.

3.4 AM-FM Mode

Since the AFM system is currently unable to calibrate for quantification of Young's modulus, data on dissipation and stiffness were acquired instead. 5 by 5 µm areas were scanned from 15 °C to 45 °C in five degree increments. The system was limited by the risk of condensation at lower temperatures and increased noise at high temperatures. To perform such an imaging run takes several hours and it is very difficult to maintain imaging quality as temperature increases. A successful run can be seen in figure 3.6.

The system produces histograms for dissipation and stiffness at each temperature, as can be seen in figure 3.7.

After fitting, the mean values are plotted to reveal a trend as temperature increases. Two such data runs are plotting in figures 3.8 and 3.9.

Dissipation increases as expected but stiffness does not have a significant increase and seems to remain relatively unchanged. Further runs must be performed to draw concrete conclusions. By overlaying the topography with sample stiffness color mapping, one can clearly see that the boundaries between lamellae are less stiff which meshes with intuition. This can be seen in figures 3.10 and 3.11.

This mode is very sensitive to noise, either introduced by humidity or the temperature control stage. As such, it is quite difficult to complete a successful run. However, despite the challenges, AMFM will remain a valuable tool for characterizing polymer crystallization.
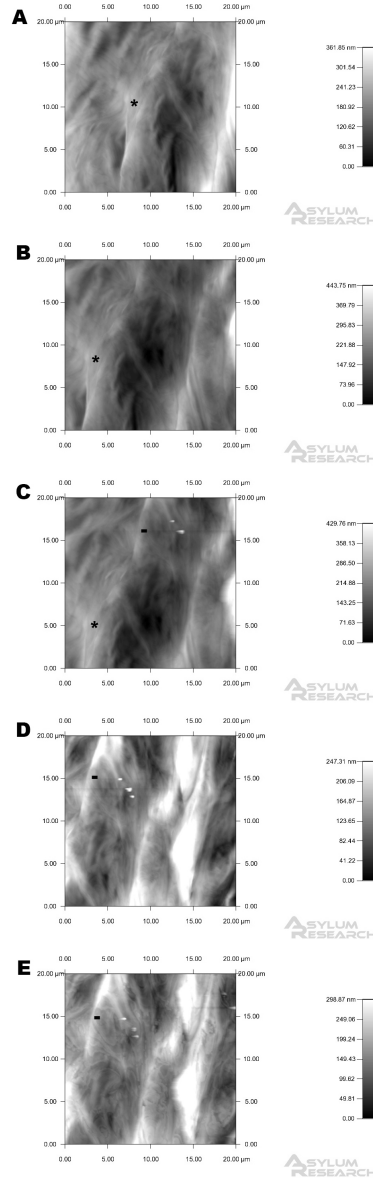
Figure 3.3: /150713/IMG0014 - 20 µm amplitude modulation mode images of PEO (MW 4000) at (A) 20 °C, (B) 20 °C, (C) 40 °C, (D) 50 °C and (E) 60 °C. (*) and (-) mark reference locations on sample surface. Note the shift in the sample due to disengaging and reengage at slightly different locations.
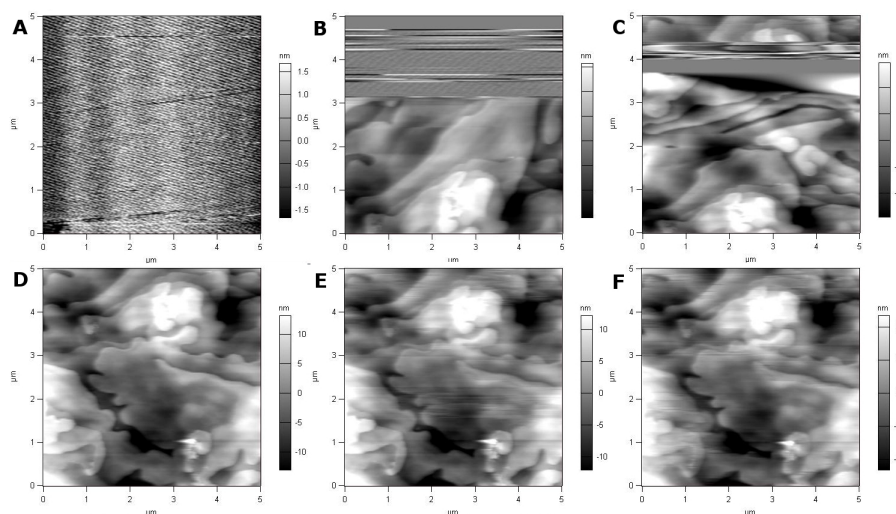
Figure 3.4: /150727 - Amplitude modulation mode height-retrace images of PEO (MW 4000) as crystallization occurs. (A) polymer melt and (F) crystallization complete.
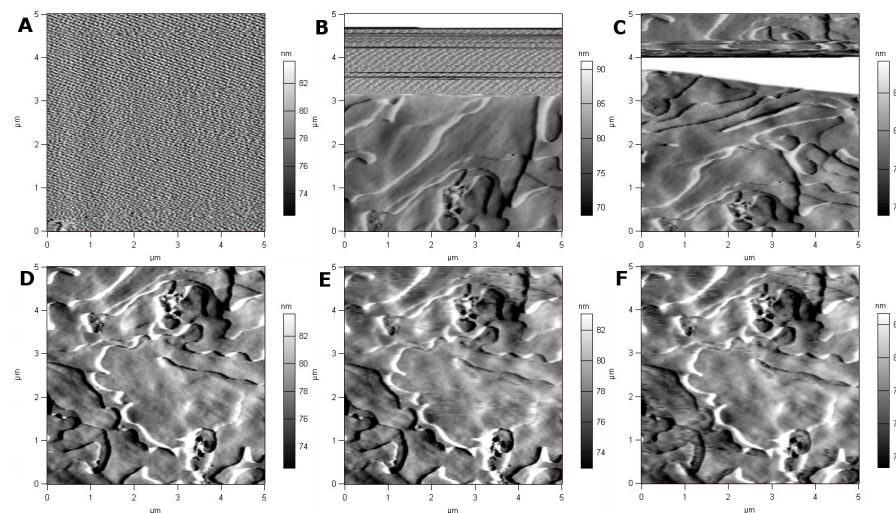
Figure 3.5: /150727 - Amplitude modulation mode amplitude-retrace images of PEO (MW 4000) as crystallization occurs. (A) polymer melt and (F) crystallization complete.
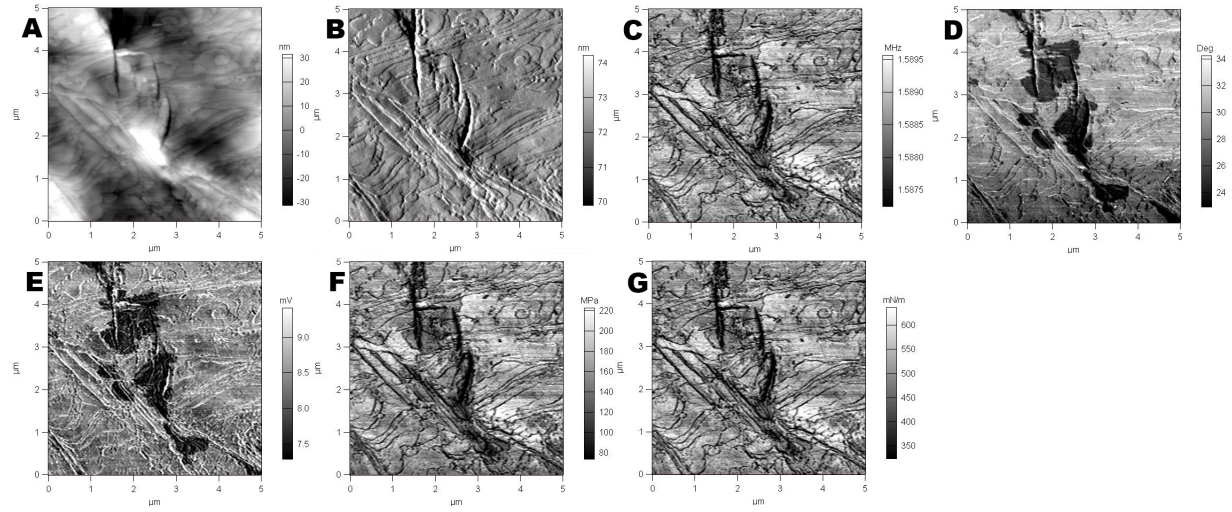
Figure 3.6: /160304/IMG0017 - Amplitude modulation - frequency modulation mode image of PEO (MW 4000) at 30 °C. (A) height-retrace, (B) amplitude-retrace, (C) frequency-retrace, (D) phase-retrace, (E) dissipation-retrace, (F) Young's modulus-retrace and (G) stiffness-retrace.
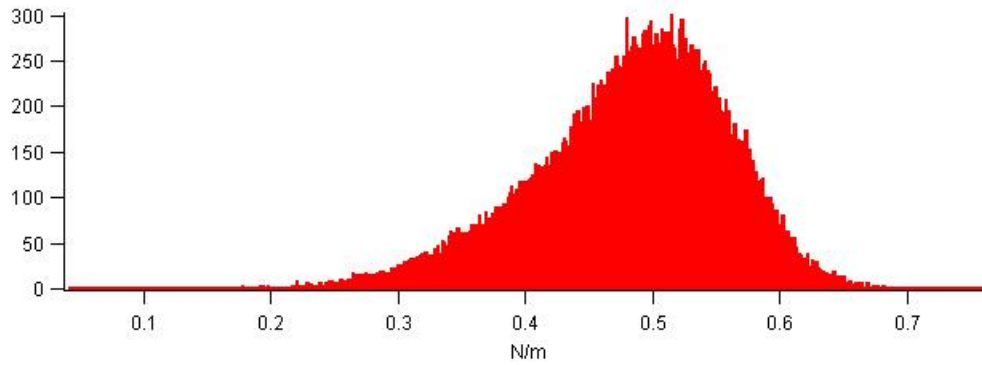
Figure 3.7: /160304/IMG0017 - Histogram of stiffness measurements on sample surface.

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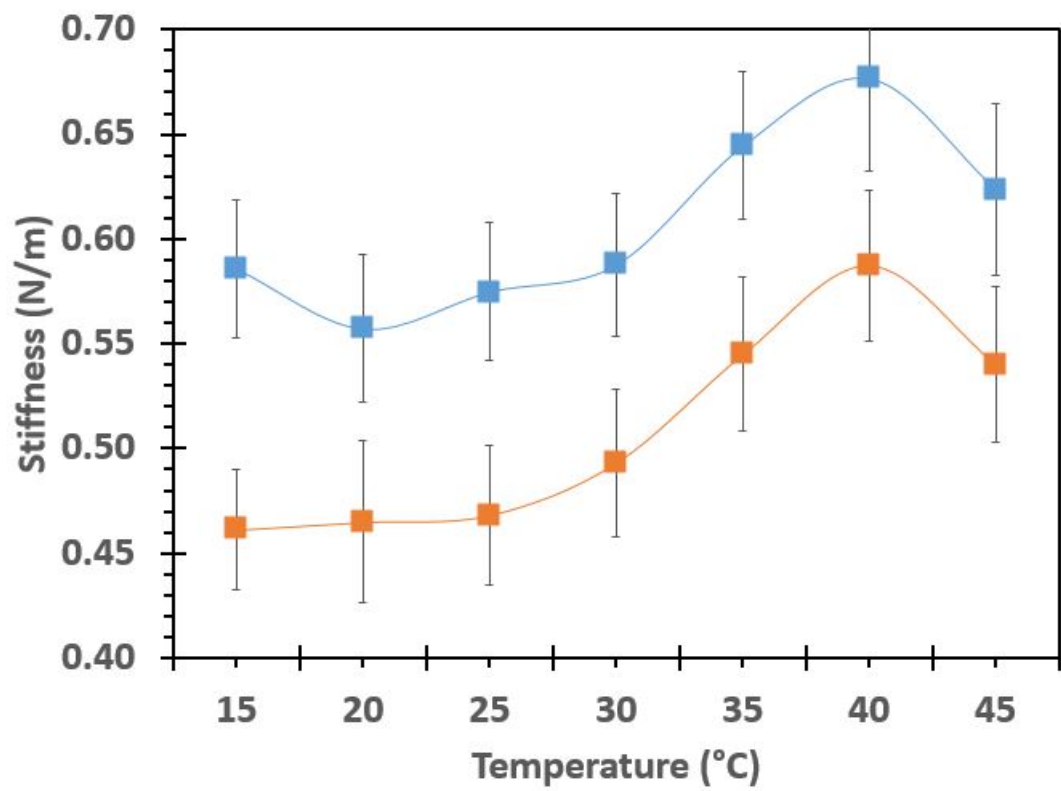
Figure 3.8: Plot of stiffness (N/m) with increasing temperature for two full sample runs.
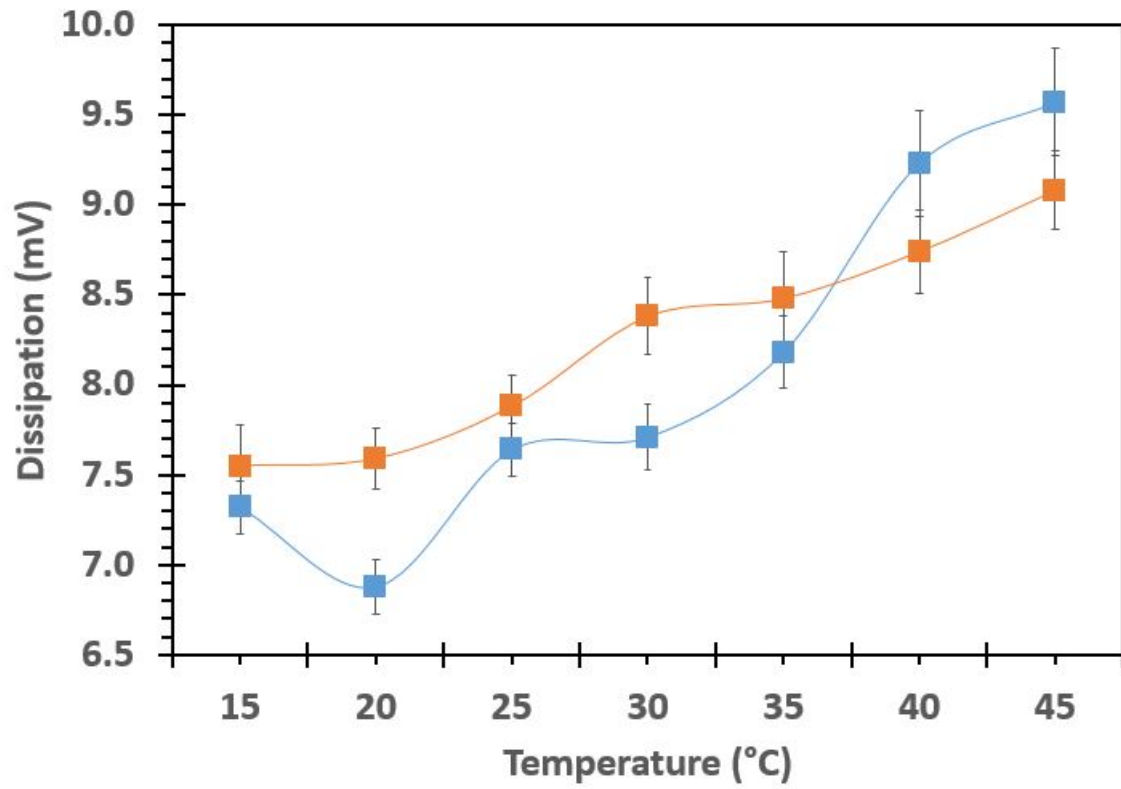
Figure 3.9: Plot of dissipation (mV) with increasing temperature for two full sample runs.
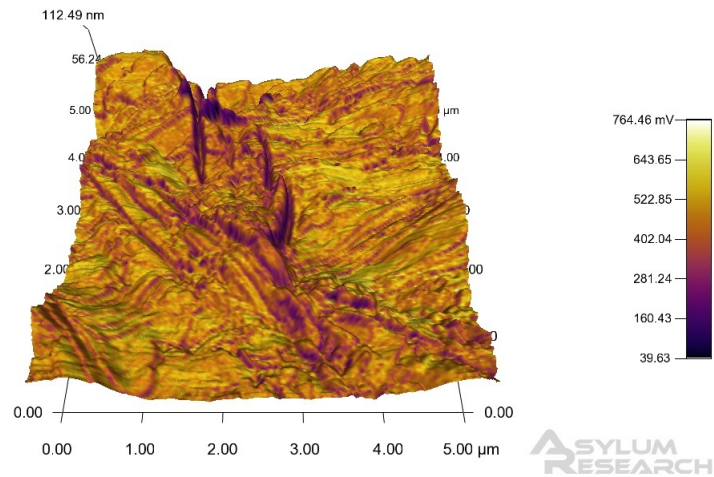
Figure 3.10: /160304/IMG0017 - Height-retrace with stiffness overlay showing lower stiffness at the grain boundary at 30 °C.
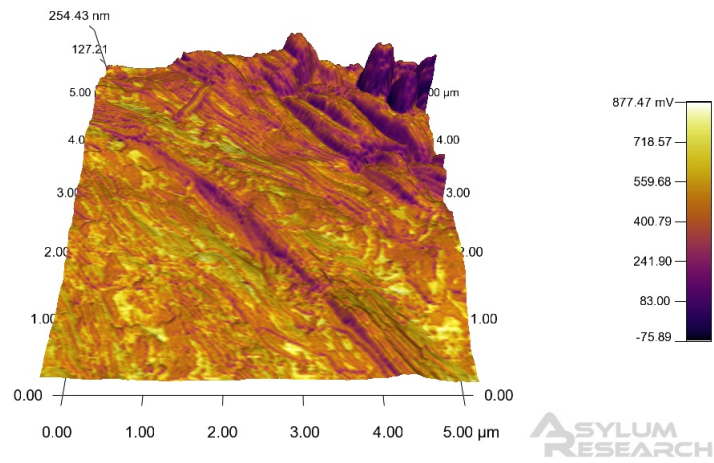
Figure 3.11: /160304/IMG0021 - Height-retrace with stiffness overlay showing lower stiffness at the grain boundary at 15 °C.

Chapter 4

Conclusion

The majority of the effort during this project was spent exploring different imaging techniques with the goal of characterizing the crystallization of PEO. Methods ranged from standard amplitude modulation mode to AM-FM viscoelastic mapping. Different sample preparation techniques were also tested. Ultimately glass cover slips proved to be the best sample holder for a small sample of PEO. They fit in the Heater/Cooler stage which makes them ideal for any work involving temperature dependence. This AFM model cannot operate at the very fast scan rates necessary to observe crystallization as it progresses. This eliminates the value of liquid AFM as we cannot observe the phase transition. AM-FM viscoelastic mapping is a new technique which has not been widely utilized in polymer research. It provides a wealth of information on the sample. Future work will involve further progress with this method. Once the system can be calibrated to quantify Young's modulus, one can measure the shift in elasticity as temperature varies. In addition, different molecular weights of PEO can be tested using the same setup.

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Appendix A

Spring Constant Calibration

1. Mount the probe.

2. Center the stage.

3. Place an infinitely hard, clean sample (glass slide) on stage with magnets.

4. Setup the mount.

   (a) Front leg should be higher than back legs which are level with each other.

   (b) Raise the camera.

   (c) Place the mount.

   (d) Lower camera until almost in contact with the mount.

5. Turn on the laser.

6. Turn on the light.

7. Start the software (do not touch the mouse while it is starting up!)

   (a) In the Master Panel, select Contact under Imaging Mode.

8. Click on the camera at the bottom of the screen to get a visual.

9. Center the probe.

10. Turn down the light.

11. Find the laser (the lowest and leftmost laser image of the four).

12. Position laser directly on the end of the probe.

13. Make the deflection slightly negative.

14. Sum should be between 5 and 7.

15. Lower the legs (back first, then the front).

16. Lower the front leg until the sample comes into focus.

17. Set the set point to slightly positive of the free air deflection.

18. Set Integral gain from 8 to 10.

19. Set scan rate to 1 Hz. For softer samples, choose a slower scan rate.

20. Click Engage.

21. Lower front leg until you hear the auditory response (the tip is in contact with the sample) and the Z-Voltage is 70 V.

22. Click the Force tab in the Master Panel.

    (a) Activate the radio button for 'red' mode.
    (b) Slide the red force distance bar all the way to the top of the white vertical Z range bar.
    (c) Choose a 'Force' distance (0.5 to 1 micrometers).
    (d) Velocity of 1 micrometer/s.
    (e) Activate the 'Trigger' from the Trigger channel pull-down menu – choose the DeflVolts channel.
    (f) Enter a trigger point value of 0.4 to 0.6 V.
    (g) Click Single Force.

23. With the force plot window active, hit ctrl + I to bring up the Igor cursor panel.

    (a) Place the Igor cursors on linear part of the free air approach (red line).
    (b) Use arrow keys to check that both cursors are set on the same trace.
    (c) Right-click on the graph and select Virtual Defl Line.
    (d) Close the Force graph window.

24. Click Single Force again.

    (a) Expand on the contact region of the curve.

    (b) Place igor cursors on either extension or retraction line (check with arrow keys).

    (c) Right-click on the graph and select InvOLS.

    (d) Record this InvOLS.

    (e) Disengage tip by clicking Stop!!!

25. Click the Thermal tab on the Master Panel.

    (a) Retract the head back a hundred microns to eliminate long-range forces.

    (b) Zero the deflection.

    (c) Click Do Thermal.

    (d) Click Stop Thermal when the plot looks like it has enough definition.

    (e) On the power spectrum plot, expand the first large peak.

    (f) Place an Igor cursor at the peak of the first resonant peak.

    (g) Type the value from the cursor (X value, Hz) into the Zoom Center parameter (kHz).

    (h) Click the Show Fit checkbox in the Thermal Tab.

    (i) Click the Fit Guess button.

    (j) Click the Try Fit button.

26. Record the Spring Constant.

Appendix B

Force Curve Acquisition

1. Mount the probe.

2. Center the stage.

3. Place an infinitely hard, clean sample (glass slide) on stage with magnets.

4. Setup the mount.

   (a) Front leg should be higher than back legs which are level with each other.

   (b) Raise the camera.

   (c) Place the mount.

   (d) Lower camera until almost in contact with the mount.

5. Turn on the laser.

6. Turn on the light.

7. Start the software (do not touch the mouse while it is starting up!)

   (a) In the Master Panel, select Contact under Imaging Mode.

8. Click on the camera at the bottom of the screen to get a visual.

9. Center the probe.

10. Turn down the light.

11. Find the laser (the lowest and leftmost laser image of the four).

12. Position laser directly on the end of the probe.

13. Make the deflection slightly negative.

14. Sum should be between 5 and 7.

15. Remove the mount.

16. Place sample on stage with magnets.

17. Replace the mount.

18. Lower the legs (back first, then the front).

19. Click in the Mode Panel:Thermal:Capture Thermal Data.

    (a) Make a box around the peak near the right.

    (b) Zoom in on peak.

    (c) Peak should be around manufacturer's specified range (good if plus or minus 10%).

    (d) Click on Fit Thermal Data.

    (e) Note frequency and spring constant.

20. Click in the Mode Panel:Tune

    (a) Set to -5% target percent.

    (b) Click Cantilever Tune.

21. Find point of interest using camera.

22. Lower the front leg until the sample comes into focus.

23. Set the set point to slightly positive of the free air deflection.

24. Set Integral gain from 8 to 10.

25. Set scan rate to 1 Hz. For softer samples, choose a slower scan rate.

26. Click Engage.

27. Lower front leg until you hear the auditory response (the tip is in contact with the sample) and the Z-Voltage is 70 V.

28. Click the Force tab in the Master Panel.

    (a) Activate the radio button for 'red' mode.

(b) Slide the red force distance bar all the way to the top of the white vertical Z range bar.

(c) Choose a 'Force' distance (0.5 to 1 micrometers).

(d) Velocity of 1 micrometer/s.

(e) Activate the 'Trigger' from the Trigger channel pull-down menu – choose the DeflVolts channel.

(f) Enter a trigger point value of 0.4 to 0.6 V.

(g) Click Single Force.

29. With the force plot window active, hit ctrl + I to bring up the Igor cursor panel.

    (a) Place the Igor cursors on linear part of the free air approach (red line).

    (b) Use arrow keys to check that both cursors are set on the same trace.

    (c) Right-click on the graph and select Virtual Defl Line.

    (d) Close the Force graph window.

30. Click Single Force again.

    (a) Expand on the contact region of the curve.

    (b) Place igor cursors on either extension or retraction line (check with arrow keys).

    (c) Right-click on the graph and select InvOLS.

    (d) Record this InvOLS.

    (e) Disengage tip by clicking Stop!!!

Appendix C

Contact Mode AFM

1. Mount the probe.

2. Center the stage.

3. Place an infinitely hard, clean sample (glass slide) on stage with magnets.

4. Setup the mount.

   (a) Front leg should be higher than back legs which are level with each other.

   (b) Raise the camera.

   (c) Place the mount.

   (d) Lower camera until almost in contact with the mount.

5. Turn on the laser.

6. Turn on the light.

7. Start the software (do not touch the mouse while it is starting up!)

   (a) In the Master Panel, select Contact under Imaging Mode.

8. Click on the camera at the bottom of the screen to get a visual.

9. Center the probe.

10. Turn down the light.

11. Find the laser (the lowest and leftmost laser image of the four).

12. Position laser directly on the end of the probe.

13. Make the deflection slightly negative.

14. Sum should be between 5 and 7.

15. Remove the mount.

16. Place sample on stage with magnets.

17. Replace the mount.

18. Lower the legs (back first, then the front).

19. Find point of interest using camera.

20. Lower the front leg until the sample comes into focus.

21. Set the set point to slightly positive of the free air deflection.

22. Set Integral gain from 8 to 10.

23. Set scan rate to 1 Hz. For softer samples, choose a slower scan rate.

24. Click Engage.

25. Lower front leg until you hear the auditory response (the tip is in contact with the sample) and the Z-Voltage is 70 V.

26. Use the hamster wheel to decrease the set point voltage and raise the tip off the surface.

27. Close the shield around the AFM.

28. Increase the set point voltage to engage with the surface again.

29. Click Do Scan.

Appendix D

Amplitude Modulation AFM

1. Mount the probe.

2. Center the stage.

3. Place an infinitely hard, clean sample (glass slide) on stage with magnets.

4. Setup the mount.

   (a) Front leg should be higher than back legs which are level with each other.

   (b) Raise the camera.

   (c) Place the mount.

   (d) Lower camera until almost in contact with the mount.

5. Turn on the laser.

6. Turn on the light.

7. Start the software (do not touch the mouse while it is starting up!)

   (a) In the Master Panel, select Contact under Imaging Mode.

8. Click on the camera at the bottom of the screen to get a visual.

9. Center the probe.

10. Turn down the light.

11. Find the laser (the lowest and leftmost laser image of the four).

12. Position laser directly on the end of the probe.

13. Make the deflection slightly negative.

14. Sum should be between 5 and 7.

15. Remove the mount.

16. Place sample on stage with magnets.

17. Replace the mount.

18. Lower the legs (back first, then the front).

19. Click in the Mode Panel:Thermal:Capture Thermal Data.

    (a) Make a box around the peak near the right.

    (b) Zoom in on peak.

    (c) Peak should be around manufacturer's specified range (good if plus or minus 10%).

    (d) Click on Fit Thermal Data.

    (e) Note frequency and spring constant.

20. Click in the Mode Panel:Tune

    (a) Set to -5% target percent.

    (b) Click Cantilever Tune.

21. Click in the Mode Panel:Main

    (a) Set scan size below 5.0 microns.

22. Find point of interest using camera.

23. Lower the front leg until the sample comes into focus.

24. Set the set point to 950 mV.

25. Click Engage.

26. Lower front leg until you hear the auditory response (the tip is in contact with the sample).

27. Continue lowering the front leg until the Zvoltage is around 30.

28. Close the shield around the AFM.

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29. Make a note of the phase.

30. Use the hamster wheel to lower Set Point by turning counter-clockwise.

    (a) You are looking for the maximum phase shift (Usually falls between 700-750 mV – Never go below 550 mV!).

    (b) You want the phase to be fairly stable, not jumping up and down.

31. Click Do Scan.

Appendix E

AM-FM AFM

1. Plug Heater-Cooler stage into Environmental Controller.

2. Environmental Controller should be attached to the Coolant Pump.

3. Plug expansion in from Coolant Pump to expansion port on AFM Controller.

4. Plug Environmental Controller into power socket.

5. Turn on the Environmental Controller.

6. Mount AC160TS-R3 probe into high-frequency cantilever holder and install into AFM head.

7. Open Asylum Research software.

8. Click ARModes:NanoMechPro:AMFM.

9. Rescan the device buses if the Heater Panel is not onscreen.

10. Use magnets to mount clean glass slide to the stage as a calibration sample.

11. Turn on the camera, zero the deflection and center the laser.

12. Approach the sample surface manually.

13. Set:

    (a) Free air deflection to -0.10 V.
    (b) Setpoint to 0.00 V.

14. In Main tab, set Imaging Mode to Contact.

15. Engage with the surface:ZVoltage at 70.

16. In Force tab, click on radio button to be in red mode.

17. Pull bar on left to the top of its range.

18. Set:

    (a) Force Distance: 1.00 micron.

    (b) Velocity: 1.00 micron/second.

    (c) Trigger Channel: DeflVolts.

    (d) Trigger Point: 0.5 V.

19. Take a force curve.

20. Use markers in software (ctrl + i) to calculate the virtual deflection line from the horizontal portion (make sure markers are on same line).

21. Take a single force curve again.

22. Use markers in software to calculate the InvOLS and record the result.

23. Disengage the tip.

24. Retract head manually.

25. Zero the deflection.

26. In Thermal tab -¿ Capture Thermal Data.

27. Expand on peak and fit peak.

28. Record spring constant.

29. Place Heater-Cooler stage in AFM and mount PEO sample.

30. In Main tab, set Imaging Mode to AC.

31. Set Scan Angle to 90.0°.

32. Autotune first frequency.

33. Center Phase1 at 90°.

34. Change second autotune low value to 1 MHz and high value to 2 MHz.

35. Autotune second frequency.

36. Center Phase 2 at 90°.

37. Move laser to maximize amplitude 2.

38. Setpoint: 1.8 V.

39. Engage with sample.

40. Capture image of sample surface with optical camera.

41. Lower setpoints such that the tip in is repulsive mode (This is very important).

42. Start scan.

43. In AMFM Panel change Drive Setpoint to 10.0 mV.

44. Adjust integral gain for height-retrace.

45. Adjust Frequency 1 gain (may need to go around 1000).

46. Adjust Drive 1 gain (may need to go around 1000).

47. Use Heater Panel to change temperature and repeat as desired.