

# Polyethylene Fiber Drawing Optimization

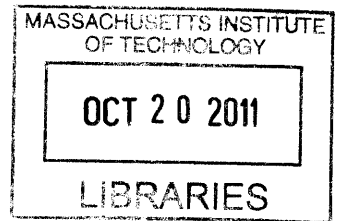
by

Vazrik Chiloyan

Submitted to the Department of Mechanical Engineering  
in partial fulfillment of the requirements for the degree of

Bachelor of Science in Mechanical Engineering  
at the

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## **Abstract**

Polymer fiber drawing creates fibers with enhanced thermal conductivity and strength compared to bulk polymer because drawing aligns the molecular chains. I optimize the polymer fiber drawing method in order to achieve polymer fibers that are drawn to lengths exceeding 1cm and develop a method to cut and store them for future experimental purposes. With lengths exceeding 1cm, starting with lengths near 0.5mm, these fibers undergo very large tensile deformations. This ensures the fibers obtained have been ultra drawn, and the polymer chains have aligned, thus enhancing the tensile strength and thermal conductivity of the fiber. By storing these fibers, I can perform experimental measurements in the future to obtain thermal conductivity values for polyethylene fibers and notice the effect of aligning the molecular chains.

Thesis Supervisor: Gang Chen

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# Table of Contents

<b>Chapter 1: Introduction</b>	<b>6</b>
<b>Chapter 2: The polymer gel suspension</b>	<b>12</b>
<b>Chapter 3: Polymer fiber drawing</b>	<b>15</b>
<b>Chapter 4: Polymer fiber storage</b>	<b>23</b>
<b>Chapter 5: Summary and Future Directions</b>	<b>31</b>
<b>References</b>	<b>33</b>

## List of Figures

1-1	Schematic showing polymer fiber drawing performed by Harfenist [4]	8
1-2	Set up of electrospinning process [6]	10
2-1	Photo showing polymer gel immersed in decalin	14
3-1	Image of the polymer fiber drawing experimental set up.	15
3-2	Close up view of the set up for polymer fiber drawing and storing.	17
3-3	Polymer fiber after the first draw step under optical microscope at 90X magnification. The length is ~ 0.5-1.0mm.	18
3-4	Image showing the Micromanipulator that holds the drawing tungsten needle mounted on top of the Motor Mike for continuous retraction.	21
4-1	Polymer fiber with heating tungsten needle in contact near the polymer droplet end under optical microscope at 90X magnification. It is being heated in order to cut it where the fiber is thick and obtain the thinner sections of the fiber for storage.	27
4-2	The polymer fiber after melting temperature was reached for the polymer fiber under optical microscope at 90X magnification. The fiber locally melted and adhered to the tungsten needle. With higher temperatures, the contact will melt off from the tungsten needle, result in separated pieces.	27
4-3	A fiber planted horizontally across the silicon oxide chip. Viewed under optical microscope at 90X magnification.	29
4-4	Same fiber planted across the silicon oxide chip. With the optical light angled, the light diffracts off of the beam and clearly illuminates the fiber's location. Viewed under optical microscope at 90X magnification.	30

# Chapter 1: Introduction

Polymers have received great interest in the scientific community due to their interesting physical properties. Polymers are typically amorphous, meaning they lack a periodic crystal structure. However, depending on conditions such as mechanical stress and temperature, the crystallinity of polymers can be altered [1]. Physical properties such as thermal conductivity and mechanical elasticity can change greatly due to the crystal structure of the polymer. Polymers are long chains of monomers that are bonded together chemically in many branches. The work presented in this thesis involves polyethylene, which is a polymer made of long chains of the monomer ethene, a simple hydrocarbon. The crystal structure of polymers can be altered through mechanical deformation. In this thesis, we explore the production of polymer nanofibers with the hope of developing high mechanical strength and large thermal conductivity materials for use in future technologies.

Bulk polymers traditionally have low thermal conductivities on the order of  $\sim 0.1 \text{ W/mK}$  due to their amorphous nature. With a random orientation of monomers, bulk polymers have low directional thermal conductivity. Common conductors, such as copper, are known to have thermal conductivities on the order of  $400 \text{ W/mK}$ . However, it has been shown that drawn polymer nanofibers can exhibit much higher values of thermal conductivity [12, 13]. The reason for this is that through the development of a polymer fiber, its molecular chains are aligned, creating a crystal structure that is better optimized for thermal transport.

The goal is to obtain nanoscale diameter fibers in order to explore the new physics that arises at the nanoscale that cannot be explained by the laws used at the

macroscopic scale. Heat no longer conducts diffusively as materials can no longer be simply modeled as continuous media at this length scale. Phonons (quantized lattice vibrations in solids) dominate heat transport, and heat is essentially conducted in a single direction in this 1-dimensional system [3]. The crystal structure of the media becomes more important as the heat conduction in certain directions will be larger than others due to the fact that at these small scales, the order of magnitude of the size of the crystal structure is now similar to the geometry of the structure, and the continuum model becomes poor.

In the ideal limit, polymer drawing would create a single chain of polyethylene molecules, resulting in a 1-dimensional conducting system. Understanding transport for this model gives us an understanding of an upper limit to the thermal conductivity that can be achieved through polymer fiber drawing. Henry and Chen used molecular dynamics simulations in order to numerically calculate the thermal conductivity of a single chain of polyethylene [3]. They obtained thermal conductivities through the Green-Kubo calculations that were as high as  $\sim 350$  W/mK and in some cases divergent for a single polymer chain suspended between two contacts. From these results, we are motivated to achieve aligned molecular chains and approach higher thermal conductivities than ever before for bulk polymers. In this thesis, I optimized the polymer nanofiber production method where polymer fibers are created by using tungsten needles attached onto Micromanipulators for micrometer scale precise control.

There are many forms of nanofiber production developed in literature today as well as different polymers used for drawing, such as poly-methyl methacrylate (PMMA). One method involves bridging polymer fibers between two droplets of polymer gel [4].

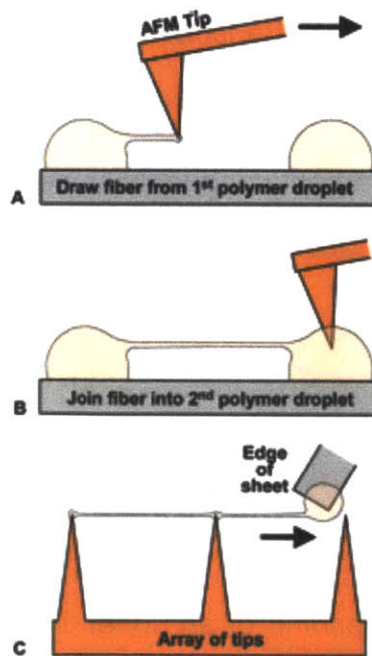


Figure 1-1: Schematic showing polymer fiber drawing performed by Harfenist [4]

As Fig. 1-1 shows, an AFM tip or some type of microscale structure is used to dip into a droplet of polymer, and then create a bridge of fiber by extending the fiber until it connects into a second droplet. In order to make long arrays, microscale structures are built and are used as collecting areas for fibers in order to create multiple fibers on a single microchip. Although this method can be more easily automated to yield many polymer fibers, the method does not actually achieve fibers with large stretch ratios because drawing is done while the polymer is still wet with solvent and is flowing out of the droplet rather than being mechanically strained. When the polymer is drawn after the solvent has dried, then we can be sure that it is the fiber that is flowing and aligning.



Another common method used for polymer drawing is solution spinning [5]. In this method, the polymer gel solution is prepared containing polyethylene dissolved in decalin (decahydronaphthalene). It is spun as a viscous fluid into a filament. This filament is then drawn in a hot oven so that the solvent evaporates, leaving a final stretched fiber. This method is also able to develop fibers in a fast automated process, but does not achieve very long, drawn fibers because there is no tensile strain achieved in the fiber to create chain detanglement and alignment.

Electrospinning is a method similar to solution spinning that produces many nanofibers in an efficient process. The viscous jet of gel is pulled into a thin fiber through the application of an electric field to generate electrostatic surface forces that pull on the fiber. This method produces fibers thinner and more uniform than normal mechanical drawing [6]. The polymer gel solution is obtained in a small syringe pump and a high voltage is applied in order to electrically charge the polymer. Once the surface charge is developed, the electrostatic repulsion between the different points of the polymer and the force due to the applied electric field will eject the polymer from the syringe. As it ejects, the fiber thins as the surface tension forces are exceeded by the electric forces, and the fiber thins and coils as it collects in a woven mat on a collector surface below:

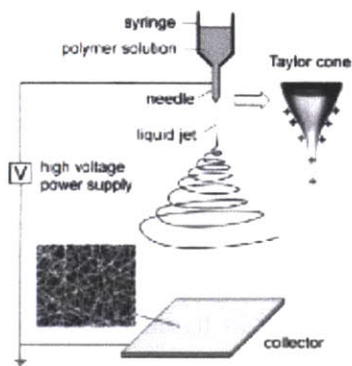


Figure 1-2: Set up of electrospinning process [6]

Electrospinning techniques for producing polymer fibers are useful in taking a solution of polymer and generating coils of fiber that have diameters ranging from as low as tens of nanometers to several micrometers. The method of production results in a mat of many fibers woven together. Although, for measurement purposes, this makes it difficult to extract a single fiber in order to measure its thermal conductivity and observe the enhancement due to the alignment of the molecular chains. With such a woven mat, the fibers can relax into coiled states rather than stay aligned. The fibers must be strained and then stored as such so that they do not fully relax and coil and become randomly aligned again.

In this work, my goal was to achieve fibers of long lengths (>5mm) with diameters that were of sub-micron scale. By beginning with an initial length of fiber, and drawing it continuously over long lengths, the polymer fiber chains will align and large stretch ratio fibers can be achieved. It is not sufficient to simply obtain a fiber that has a diameter smaller than 1 micron in order to enhance the properties of the polymer. Ideally, the fiber should be axially strained in order to draw the tangled polymer chains into a one dimensional, aligned nanofiber. We explore the development of such fibers through

micrometer-diameter tungsten tips as drawing needles with the precision of motor-controlled stages and Micromanipulators.

After nanofiber production, it is desirable to have a method of storage of these nanofibers for future use. I have developed a method for locally cutting the polymer fiber in order to extract a quality section of it for storage. The desired section of the fiber is cut and planted onto silicon oxide chips and stored for future experimental use. One experimental goal is to measure the thermal conductivity of these fibers at various temperatures to view how temperature and the alignment of the polymer chains affect the thermal conductivity of polymers. Theoretically modeling and calculating transport properties for polyethylene fibers is difficult due to the unpredictable crystal structure formed after drawing the fiber. With experimental results, we can get a better understanding of the effects of molecular alignment and give us better insight into the physics at this length scale.

In this paper, chapter 2 will discuss how the polymer gel suspension is made from which the fibers are drawn. Chapter 3 will describe the ideal experimental method for fiber drawing in order to create long, high stretch ratio fibers. Chapter 4 will discuss the methods developed in storing the fibers on microchip devices, and chapter 5 will conclude the paper and discuss future directions that can be taken with this research.

## Chapter 2: The Polymer Gel Suspension

In order to draw polymer nanofibers, first a gel suspension must be prepared. The difficulty here lies in the fact that since polymer bonds are quite strong and the molecules themselves are very large due to the numerous monomers bonded to each other, it is difficult to find a solvent that can dissolve polyethylene at temperatures near room temperature. Possible solvents that can dissolve polyethylene include aromatic hydrocarbons such as benzene, toluene, and xylene as well as alicyclic hydrocarbons such as cyclohexane, tetralin, and decalin [7]. The most common solvents used are decalin and xylene due to the fact that they are safer to handle than the others. At temperatures around 150 °C, the polyethylene powder begins to dissolve. For our experiment, decalin (decahydronaphthalene) is used to dissolve the polyethylene since it is the safest compound.

Polyethylene is a common choice for developing polymer nanofibers due to the simple monomer structure of ethene. Other polymers have also been used in drawing such as polymethyl methacrylate (PMMA), polyvinyl pyrrolidone (PVP), polyvinylidene fluoride (PVDF), and others [6]. Polyethylene is used in this work because of its simple structure. Made of ethene monomers, a single ideal chain would consist of a string of carbons as a backbone. These carbons would be double bonded to each other, and also have two single bonded hydrogen molecules. This simple structure allows for straight chains to enhance the longitudinal directional heat transport as well as mechanical strength of the fiber. Since the polymer fiber is mechanically drawn, having the simplest structure would allow for the least problems with viscosity of the polymer

when drawing. With more complex monomers structures found in other polymers, even higher temperatures and more toxic chemicals would be needed in order to dissolve the polymer and create the appropriate gel suspension.

Heating and dissolving the polyethylene powder (ultra high molecular weight polyethylene) takes place in an argon glove box in order to prevent oxidation of the polymer. The oxidation of the polymer results in degradation, thus decreasing the polymer quality. "Although all polymers degrade at high temperatures in the absence of air, degradation is almost always faster in the presence of oxygen" [8]. Oxidation will cause bond breaking in the polymer chain and thus weaken the structure of the system.

A degraded gel makes polymer drawing more difficult. There will be damage to the molecular chain due to oxidation, and so the chain length will, on average, be shorter. With shorter chains, the tensile strength of the material will be lower, and this will cause problems for polymer drawing. For ideal drawing, the material should be able to handle tensile stress without breaking so that the polymer flows and the chains detangle. If the chains are weak, then even if the pulling of the fiber is very slow, the monomers will break apart and the fiber will break prematurely before achieving high draw ratios.

A 0.8% by weight of ultra high molecular weight (UHMW) polyethylene (molecular weight between 3 and 6 million, from Alfa Aesar) in decalin (decahydronaphthalene, from Alfa Aesar) solution is prepared to create the gel suspension similar to the work by Shen [2]. Polyethylene powder is massed and placed in an appropriate volume of decalin to achieve this mass percent, and the container holding this solution is closed tightly to prevent decalin vapor leakage and placed into

the Argon chamber with a hot plate. A magnetic stirring rod is placed in the solution to provide mixing while the solution is heated to facilitate the solubalisation of the polyethylene powder. At solution temperatures near 150 °C, the polyethylene dissolves and the solution becomes a very viscous clear gel. The container is then taken off of the hot plate to cool in the argon air for about 10 minutes, and then quenched in water overnight in order for the gel suspension to nucleate out of the solution. Within an hour, the gel suspension will be complete, and the polymer nanofiber drawing can begin.

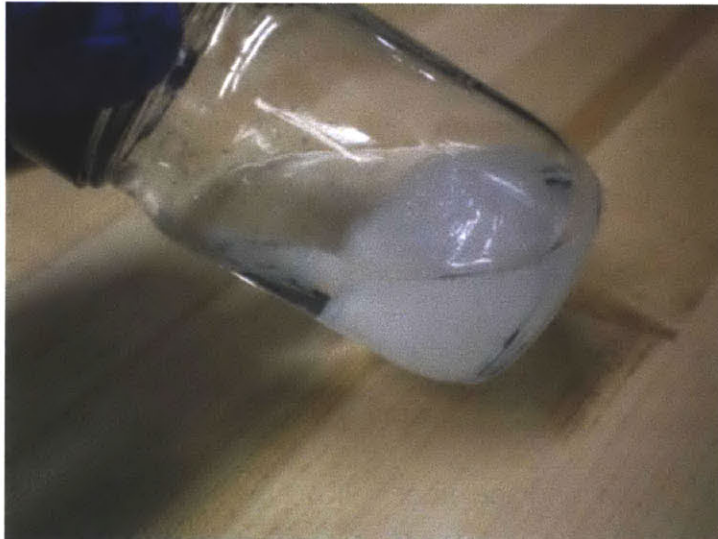


Figure 2-1: Photo showing polymer gel immersed in decalin

## Chapter 3: Polymer fiber drawing

In order to draw polymer nanofibers, the appropriate thermal conditions need to be maintained. The drawability of the fibers is highly dependent on the temperature since that affects both the viscosity of the polymer fiber as well as the evaporation rate of the decalin solvent. The ideal temperatures I have discovered to optimize the drawing success rate is to heat the air around the fiber to around 60 - 70 °C while the actual platform on which I set the polymer droplet on is around 90-95 °C. A small glass slide with a resistor is attached to this platform so that an electric current can be run through the resistor in order to produce ohmic heating.



Figure 3-1: Image of the polymer fiber drawing experimental set up.

In Fig. 3-1, we note the experimental set up used to draw the polymer fibers. On the left is a Micromanipulator on which lies the small glass heater. On the right is the Micromanipulator on which the drawing tungsten needle is attached. Tungsten needles with diameters on the order of 1 micron are used in order to draw polymer fibers. The hot plate provides heating from below to heat the air around the fiber. The optical light provides better illumination in order to see the thin fiber under the optical microscope. The black and yellow ventilation tube provides ventilation of the decalin fumes. As the decalin evaporates from the fiber during drawing, the fumes are ventilated away for the safety of the user. Also, the forced convection as a result of the suction of the air provides a more stable air temperature around the fiber. Without the forced convection, the hot air around the fiber would experience buoyancy currents driven by local thermal gradients, and create larger chaotic fluctuations of the temperature around the fiber. The lack of stable air temperature near 70 °C would prevent successful drawing of polymer fibers.



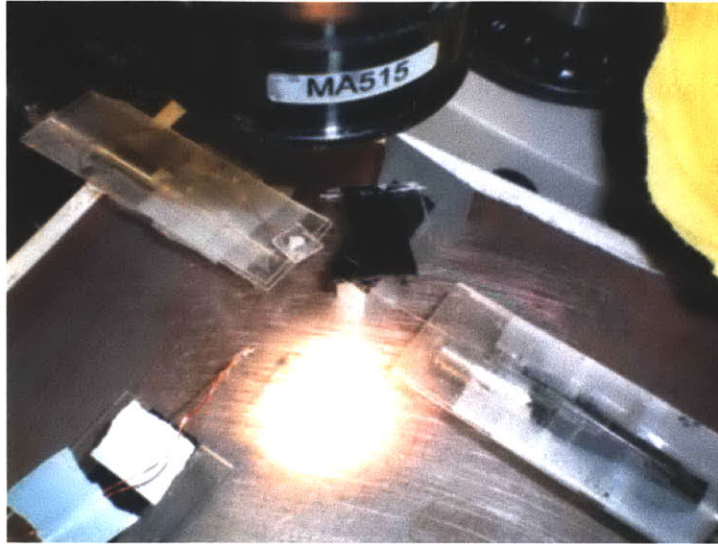


Figure 3-2: Close up view of the set up for polymer fiber drawing and storing.

Fig. 3-2 shows the set up for the polymer fiber drawing and storing processes. On the left is the small glass slide heater. On the right is the tungsten needle on top of the manipulator. In between is the black silicon oxide chip on which the fiber will be planted. In the bottom left is the heating tungsten needle that melts the fiber to plant it using an RTD resistor. Below the set up is a hot plate with a copper sheet covering it to provide uniform air heating for polymer drawing.

The concentration of decalin is crucial in the beginning, when first making contact with the polymer droplet. The first contact that the drawing needle makes with the polymer droplet determines how well the polymer adheres to the drawing needle. Contact must be made once the right amount of decalin has evaporated since the amount of decalin affects the viscosity of the gel. Initially, the viscosity of gel will be too low for any of the polymer to adhere to the tungsten tip. However, if one waits too long, the gel will dry up and the decalin will completely evaporate, leaving a hardened residue

of polyethylene, and the tungsten needle will not be able to penetrate the gel. The ideal time after placing a small droplet of gel onto the small heater is ~10 seconds, but often judgement is made by witnessing the quality of the fiber under the optical microscope and how it reacts to contact with the tungsten needle.

When the initial contact is made with the polymer droplet, the tungsten tip is retracted quickly (at a speed of about 200 microns per second), created an initial fiber that is rather thick and is still experiencing evaporation of the decalin. During drawing, I can typically see the decalin as it evaporates under the microscope while drawing the polymer. When the decalin has evaporated, it leaves a fiber of about 0.5mm long between the polymer source droplet and the tungsten drawing needle. From here, we can begin to retract further in order to draw a much longer fiber.

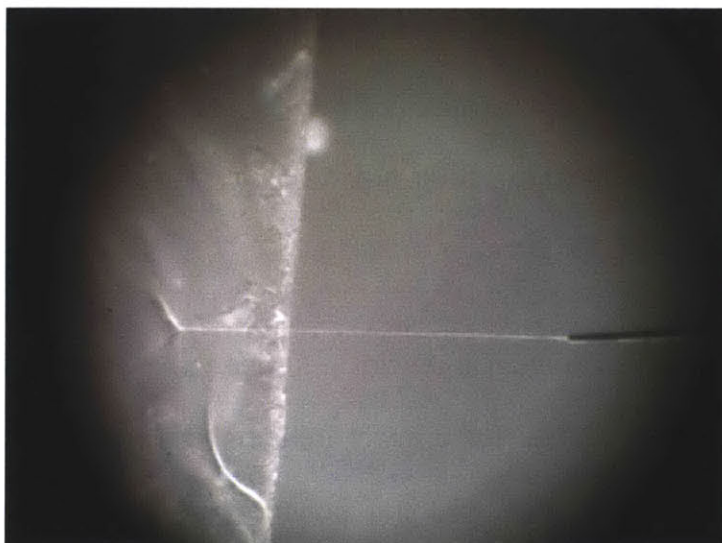


Figure 3-3: Polymer fiber after the first draw step under optical microscope at 90X magnification. The length is between 0.5mm and 1.0mm.

The goal of the initial draw is to obtain a stable fiber adhesion on the tungsten needle and at the droplet source. I need to have a strong enough base at both ends so that when there is tension placed on the fiber, it does not fail at its two ends but instead the tension causes the fiber to elongate and the polymer chains to detangle and align. After the first draw is achieved and the decalin evaporates, I then begin the main draw, which can take the fiber from a length of 0.5mm up to lengths of 15mm. It is in this process that the fiber will experience the actual alignment of its chains as it lengthens and its diameter decreases. Before I begin drawing, I wait until both ends of the fiber have completely dried from the decalin evaporation. This is done to ensure that by retracting the tungsten needle, I am mechanically straining the fiber and it experiences lengthening due to deformation of its polymer chains rather than pulling more polymer out from the droplet source.

The retraction of the fiber after the ends have dried will cause the fiber to thin and lengthen. We can obtain an order of magnitude estimate of the final diameter by assuming simple volume conservation during the fiber's tensile deformation. Measuring the initial and final lengths of the fiber under the microscope is straightforward using a built in ruler in the optical microscope's eyepiece. By approximating the fiber as a simple cylinder, we obtain for the volume:

$$V = \frac{1}{4}\pi LD^2 \quad (1)$$

After making an estimate on the initial thick diameter of the fiber under the microscope, I can obtain an estimate for the final diameter of the fiber from assuming volume conservation of the fiber under deformation:

$$V_{initial} = V_{final} \quad (2)$$

Finally obtaining an approximation for the final diameter through the relation:

$$\frac{D_i}{D_f} = \sqrt{\frac{L_f}{L_i}} \quad (3)$$

During the second main draw when the fiber ends have fully dried and I can be sure that the fiber is actually deforming, I can make an order of magnitude estimate of the ratio of initial to final diameters. Typically, I begin the second step of the drawing with a fiber that has a length of approximately 0.5mm. In the end, I have achieved fibers with lengths up to 15mm. The ratio of lengths of about 30 results in a diameter ratio of approximately 5.5. This means that my initial diameter will be more or less 5 times larger than the final diameter. This simple order of magnitude estimate useful in giving an order of magnitude understanding of how small of a fiber can be achieved when starting with a certain initial diameter so that fibers can be pre-selected in the beginning to be thin enough to achieve sub-micron final diameters. If I begin with a fiber on the order of 1 to 5 microns in diameter, it is feasible to reach a final fiber diameter that is less than 1 micron.

During the second drawing step, which takes the fiber from a length of ~0.5mm up to lengths of 15mm, the drawing speed must be chosen in order to minimize the stress to the fiber while elongating the polymer strands. Often, the fiber will break somewhere near the middle since it begins to neck rapidly in one region. This location is the weakest along our polymer fiber bridge, and so it will continue to neck until it breaks there. The optimal speed I have discovered that yields long stable fibers is approximately 5 microns/second for the retraction speed of the drawing tungsten needle.

To draw the fibers at a controlled speed, I use a MotorMike, which is just a motorized platform that allows me to move the drawing tungsten needle forward/backward at fixed speeds on the order of micrometers per second. This allows for a continuous rate of retraction as opposed to using one's hands to turn the knobs of a Micromanipulator. With constant speed, there is minimal shock to the fiber from sudden accelerations, and at the slow speed of 5 microns/second, this gives the fiber enough time to flow and elongate without breaking.

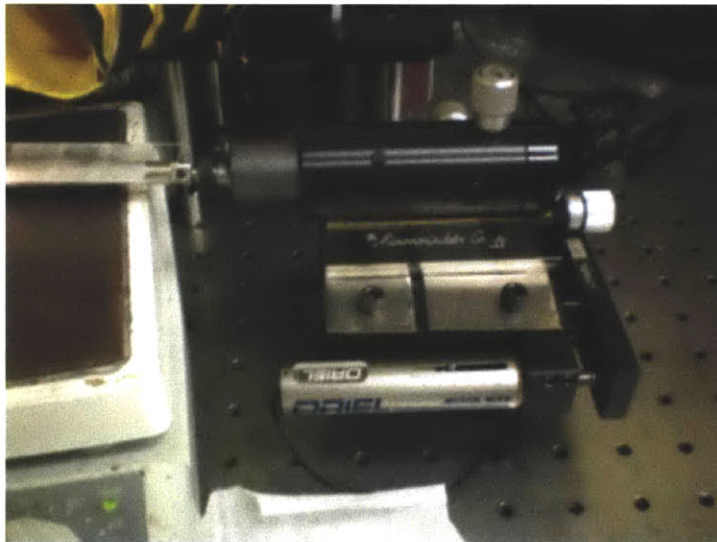


Figure 3-4: Image showing the Micromanipulator that holds the drawing tungsten needle mounted on top of the Motor Mike for continuous retraction.

Once the second drawing phase begins at the set speed of 5 microns/second, the MotorMike is allowed to run continuously until the fiber of desired length is achieved. At times, I will stop the retraction in order to adjust the lateral alignment of the fiber and the drawing needle so that when the tungsten needle retracts, it is actually retracting

longitudinally and not offset by an angle. This minimizes the shear stresses that can be generated by stretching at an angle and will allow for a more stable fiber to be formed.

After the fiber has been elongated to the desired length, the tungsten drawing needle is moved in the forward direction in order to release some tension in the fiber. The hot plate is turned off, and the small resistive heater is turned off, as well as the suction from the ventilation piping. As the thermal conditions around the fiber cool, it is important to make sure that the fiber is slack. When the material cools, it will contract to some degree, and if the fiber is left the same way once done drawing, it may contract too much and break. Therefore, enough freedom is given for the fiber to contract but at the same time maintain the fiber length so that the polymer chains do not recoil. With the drawing step complete, we can move on to the storage phase so that these drawn polymer fibers can be used for experiments.

## Chapter 4: Polymer fiber storage

After obtaining a fiber of a desired length and thickness, it is useful to have a storage method in order to access these fibers later for experimental measurements. The method developed in my project has been to plant the fiber onto a silicon oxide chip. The method developed here for storage can also be used in the future to plant the fibers onto the microchip devices developed by Dr. Mavrokefalos in order to measure the thermal conductivity of individual polymer fibers [9]. By having the drawn fiber planted onto a silicon oxide chip, it can always be retrieved later for a given measurement. Also, small sections of the fiber can be extracted so that for a given ~5mm of fiber that has been planted onto a silicon oxide chip for storage, there can be many samples extracted for thermal conductivity measurement.

If the fiber is planted properly, it will remain attached due to surface forces. At this small scale, the fiber adheres to the chip through van der Waal forces. Silicon oxide chips are developed as the chips for storage because they match the material used for the suspended micro-device developed by Dr. Anastassios Mavrokefalos. These microchips can eventually be used in order to measure thermal conductivity of such nanostructured samples as well as perform structural characterization of the same sample.

In order to plant a fiber onto a chip and store it, the fiber needs to be able to be cut and placed onto a chip so that it bonds and adheres to the chip. However, cutting the fiber is not a straightforward process due to the length scales we are dealing with. With a fiber of diameter on the order of nano- and micro-scale, with a length in the

millimeter scale, to be able to achieve localized cutting requires tips that are sharp at the nanoscale. Even still, with mechanical cutting, one would have to somehow isolate the fiber so that it does not bend and experience shear while cutting and instead break elsewhere.

At first, mechanical means were used to cut the polymer fibers using tungsten tips similar to the ones used to draw the fiber. However, the tips were not sharp enough to cut the fibers and would cause too much bending of the fiber during the cutting attempt and would break the fiber at undesired locations. Therefore, we turned to using localized melting to cut the fiber. The major difficulty with trying to melt the fiber so that it becomes a liquid in a localized region and breaks into two pieces is the fact that the thermal conductivity of the fiber is high. Due to the polymer fiber drawing process, we have in theory increased the polymer fiber thermal conductivity, and so it will be able to transport heat away very quickly. Therefore, we used a tungsten needle similar to the ones used for drawing with an RTD resistor attached in order to provide a hot tip. With this hot tip, we could make good surface contact with the fiber and ensure that it would melt at the location where the tip and the fiber met.

In order to plant the polymer fiber onto the silicon oxide chip, the following steps are implemented: the fiber is brought down onto the chip while remaining partially taut, the fiber is melted onto the chip at each end of the chip, and finally the fiber is melted near those ends to achieve a fiber that is separated from the tungsten needle and the polymer droplet source. In order to melt the polymer, the fiber is brought to 150 °C, and the polymer becomes liquid in a very localized region and it solidifies quickly after flowing onto the chip and making better contact with the chip. Since the heating needle



is only brought to around 150 °C, only the point very close to the contact point of the fiber and needle reaches melting temperature for polyethylene and melts. From experience, this length of melting is only on the order of 100 micrometers or less. By flowing onto the chip and then solidifying, the polymer adheres even stronger to the storage chip.

One concern associated with planting a drawn fiber is being able to locally cut the fiber without causing much damage to the rest of the fiber. The quality of the fiber near the middle should be maintained while still being able to separate a section of the fiber to plant it on the silicon oxide chip. The fiber is brought into contact while still partially taut in order to maximize the area of fiber that is contact with the fiber. This increases the adhesion between the fiber and the silicon oxide chip due to the larger surface forces when more of the fiber is in contact with the chip. Also, when partially taut, the fiber is less likely to coil with itself and allow for polymer chains to coil. Also, in a lengthened line, it is easier to extract a section of the fiber in the future for experimentation instead of when the fiber is coiled upon itself.

The fiber is melted at the two ends of the chip to ensure that it stays planed on the chip. Since the melting range is only on the order of 100 micrometers, for a fiber length of ~ 5 millimeters on the chip, this is a negligible length. The polymer has a melting temperature on the order of ~150 °C. To achieve this temperature at the tip of the tungsten needle, tungsten needles from GGB Industries were used. These tungsten tips have thick tungsten tip shafts on the order of several millimeters and converge down to a cone of tip with thickness on the order of a micron. The small size of the tip allows for localized heating of the polymer fiber, and the thick shaft allows for higher

heat transfer along the shaft. To heat the tungsten needle, a simple RTD resistor is attached to the shaft of the needle and heated to temperatures around 200 °C, allowing for the heat to conduct several millimeters down the length of the needle to the tip. With tips that have too small of a shaft diameter, the thermal conductance is so small that the convective heating will prevent the tip to achieve high enough temperatures to melt the polymers. Even with a thick shaft, with a simple fin model, assuming a shaft of 1 millimeter in diameter, the distance from the tip that the RTD can be mounted and still allow for the tip to reach near melting temperature is only on the order of several millimeters.

The fiber melting method was tested on a drawn fiber as a proof of concept in the beginning. By turning up the voltage input slowly, the temperature of the tungsten needle was raised, and noted at what point the polymer fiber melted and how it melted at the contact point. We wanted to achieve localized melting and wanted to understand whether this could be achieved. Fig. 4-1 shows the heating tungsten needle in contact with the polymer near the polymer droplet end and Fig. 4-2 demonstrates the aftermath after heating the tungsten needle to the melting temperature.



Figure 4-1: Polymer fiber with heating tungsten needle in contact near the polymer droplet end under optical microscope at 90X magnification. It is being heated in order to cut it where the fiber is thick and obtain the thinner sections of the fiber for storage.

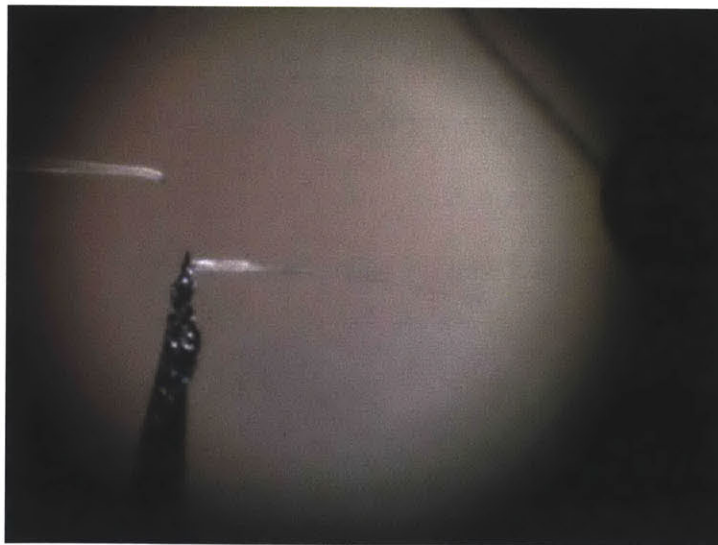


Figure 4-2: The polymer fiber after melting temperature was reached for the polymer fiber under optical microscope at 90X magnification. The fiber locally melted and adhered to the tungsten needle. With higher temperatures, the contact will melt off from the tungsten needle, result in separated pieces.

With the RTD resistor heating the tip of the tungsten needle, this tungsten needle is mounted onto a Micromanipulator in order to have the precise control needed to melt the fiber in a very localized region. A Micromanipulator is a stand that allows for 3-dimensional motion with resolution on the order of micrometer scale. While viewing the fiber on the chip under the microscope, the heating needle is brought from above onto the chip into it presses down onto the fiber and makes good contact. Good contact is needed to minimize the contact resistance between the polymer and tungsten surfaces. The voltage source providing current to the RTD resistor is slowly turned on, heating the tungsten needle at a slow rate. This is done to minimize thermal shockwaves generated from a very sudden impulse heating that could melt the fiber abruptly and uncontrollably. With quick increases in the voltage supplied, the polymer fiber typically melts rapidly as the material does not have enough time to slowly conduct the excessive heat away. With slow heating, eventually the melting temperature is reached, and by dragging the heating needle over the fiber, localized melting is achieved and the polymer melts onto the silicon oxide chip. After solidifying, the strong bond between the fiber and the chip is established and we can be sure that the fiber will stay on the silicon oxide chip.

Once the fiber is planted and melted onto the chip, all that remains is to cut away the fiber just off the edge of the chip so that it is no longer connected to the polymer source or the drawing tungsten needle. This is done simply in the same manner that fiber was melted on the chip. The heating tungsten needle tip is brought in contact with the fiber, and the temperature of the tip is slowly increased until melting temperature is reached, and the fiber locally melts into two pieces. This finalizes the process, yielding a fiber

that has its ends melted onto a silicon oxide chip and the middle region of ~5mm still high quality drawn fiber that can be used for experimentation.

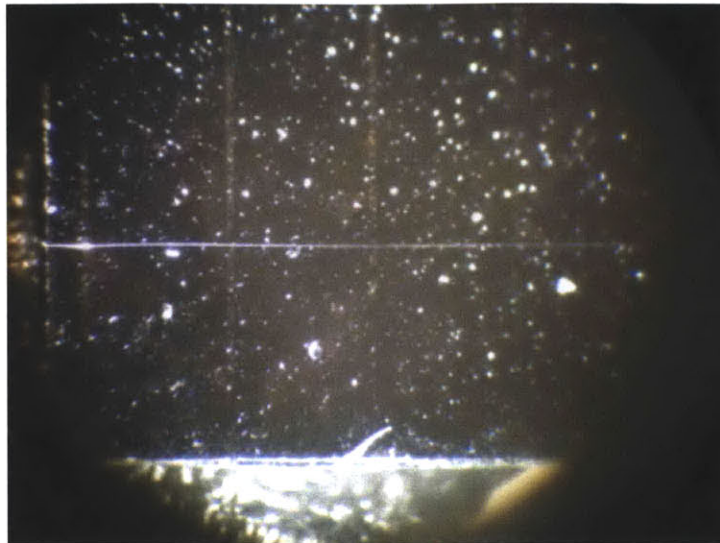


Figure 4-3: A fiber planted horizontally across the silicon oxide chip. Viewed under optical microscope at 90X magnification.

We see an example of such a planted fiber in Fig. 4-3. With a fiber successfully planted on the chip, we can draw more fibers and plant them on this chip as well so that a single chip can contain several fibers so that extracting a section of fiber is convenient in the future.

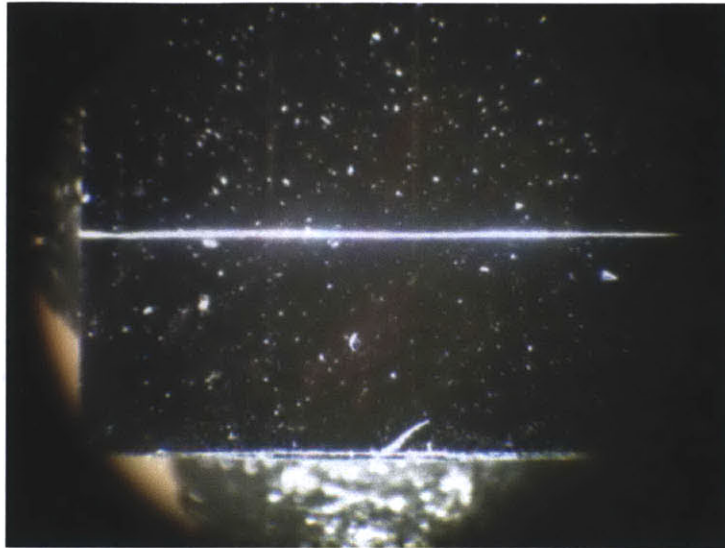


Figure 4-4: Same fiber planted across the silicon oxide chip. With the optical light angled, the light diffracts off of the beam and clearly illuminates the fiber's location. Viewed under optical microscope at 90X magnification.

## Chapter 5: Summary and Future Directions

In this study, I have optimized the polymer fiber drawing method to produce very long fibers on the order of 1-2 millimeters in length with nano- to micro-scale diameters (Chapter 3). With this method, we create ultra drawn polymer fibers that have undergone large tensile deformation to align its molecular chains. I have developed an approach to locally cut the fiber and plant it onto silicon oxide microchips in order to store them for future experiments (Chapter 4). The fiber storage method also serves as a proof of concept for the future in order to plant the fibers onto the microchip devices prepared by Dr. Mavrokefalos and measure the polyethylene fiber thermal conductivity [9].

With highly aligned polymer nanofibers, the mechanical strength and the thermal conductivity are enhanced due to the alignment of the polymer chains. Measuring the enhancement is interesting in order to be able to see a quantitative measure of the effect of polymer chain alignment. As the chain aligns, the crystal structure of the polymer gel is altered, and the system becomes more of a 1-dimensional system. Shen has demonstrated that experimentally, these aligned fibers have thermal conductivity as high as  $\sim 100$  W/mK [2]. Henry and Chen have demonstrated through simulations that the thermal conductivity of a single polymer chain can achieve very high values such as  $\sim 350$ W/mK [3]. Although realistically, one cannot achieve a pure single chain, this is an ideal limit, and demonstrates that the mechanical alignment towards this one dimensional limit will enhance the thermal conductivity by several orders of magnitude [3].

A future goal is to be able to experimentally measure the thermal conductivity of the drawn polymer fibers in order to verify the theoretical results. Using the suspended microchips developed by Dr. Mavrokefalos and a cryostat, the thermal conductivity of these chips can be measured at various temperatures to also get an understanding of how temperature affects the system. Now that the long fiber can be achieved, as well as a method developed to cut and plant the fiber, it is possible to similarly cut and plant the fiber across the membrane of the suspended microchip and measure its properties. If the desired enhancement in thermal conductivity demonstrated experimentally, we hope that this research can provide motivation for further work in developing polymer fibers and their use in thermal systems as a cheaper alternative to metals.



## References

- [1] Krimm, Samuel, and Arthur V. Tobolsky. *Quantitative X-Ray Studies of Order in Amorphous and Crystalline Polymers. Quantitative X-Ray Determination of Crystallinity in Polyethylene*. Journal of Polymer Science. 1950, Vol. VII, No. 1, 57-76.
- [2] Shen, Sheng. *Probing Extraordinary Nanoscale Energy Transfer Using Bimaterial Microcantilevers*. Cambridge: Massachusetts Institute of Technology, 2010.
- [3] Henry, Asegun and Gang Chen. *High Thermal Conductivity of Single Polyethylene Chains Using Molecular Dynamics*. Physical Review Letters. PRL 101, 235502 (2008).
- [4] Harfenist, Steven A., et al. *Direct Drawing of Suspended Filamentary Micro- and Nanostructures from Liquid Polymer*. Louisville: Nano Letters, 2004. Vol. 4 No. 10.
- [5] Smith, Paul, and Piet J. Lemstra. *Ultra-high-strength polyethylene filaments by solution spinning/drawing*. Journal of Materials Science, 1980. 15.
- [6] Li, Dan and Younan Xia. *Electrospinning of Nanofibers: Reinventing the Wheel?*. Advanced Materials. 2004, 16, No.14.
- [7] Sano, Akira. Process for the Production of Polyethylene Materials. Nippon Oil Co., Ltd., assignee. Patent 5,026,511. 25 June 1991.
- [8] Grassie, Norman, and Gerald Scott. *Polymer Degradation and Stabilisation*. N.p.: Cambridge University Press, 1988. *Google Book Search*. Web. 13 May 2011. <<http://books.google.com/>>.
- [9] Mavrokefalos, Anastassios Andreas. *Thermoelectric and Structural Characterization of Individual Nanowires and Patterned Thin Films*. Austin: The University of Texas at Austin, 2008.