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Induced Asymmetric Deformation of Silver Coated Micron-Sized Wires

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Induced Asymmetric Deformation of Silver Coated Micron-Sized Wires

An Honors Thesis

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The Department of Chemistry

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Bachelor of Science, with
Honors in Chemistry

by

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Abstract

The stimuli response of a polymer – metal bilayer architecture was investigated. This solvent activated system showed a dynamic response when exposed to a particular solvent.

Polymer wires were fabricated using a glass capillary array (GCA) as a template. The synthesized wires were then sputtered with silver and exposed to dichloromethane (DCM). The solvent activated response results in a number of physical distortions of which the circular deformation was the most predominant. The thicknesses of the metal coating and the direction of the solvent front were studied in an effort to determine their relationship to the observed wired deformations.

Keywords: Bilayer, Dichloromethane, Glass capillary array, deformations, sputtering

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Introduction

Polymers

One of the most memorable breakthroughs in polymer chemistry was the development of vulcanization in 1844 for which Charles Goodyear obtained a US patent[1]. This event is considered to be one of the major starting points of polymer chemistry. Interestingly it was recently reported that Ancient Meso Americans used polymers for many different purposes and were even able to chemically treat it in order to enhance certain properties[2]. These ancient cultures used polymer materials for sandals, game balls and containers long before the

Figure 1 - Mesoamercain rubber game ball

formal discovery of polymers. Today polymer materials are an essential part of our lives. Polymers can be found everywhere from clothing to computers. Different polymer materials are used for different purposes depending on their properties. The development of this field since the late 1800 has allowed the creation of a myriad of polymer materials for very specific purposes.

Polymers can be categorized as naturally occurring or synthetic, and in some cases a combination of the two. Common examples include rubber which is extracted from trees and polyethylene which is synthetically made and is used to made containers. Because of their use of thousands of applications, polymer materials are a big part of world economy. Currently 90 million pounds of synthetic polymers are produced within the

United States every year. Moreover 24 billion dollars of plastics are exported and 14 million are imported every year[3].

As its Greek name implies, a polymer can be described as a large molecules composed of a number of smaller molecules joined together. According to this description a large piece of polymer such as a tire can be considered a single molecular entity. The formal IUPAC definition of a polymer is "a molecule of high relative atomic mass, the structure which essential comprises the multiple repetitions of units derived, actually or conceptually from molecules of relative molecular mass"[4].An example of a polymer is polypropylene which consists of thousands propylene monomers bonded together.

Bonds between polymers normally form between two different chains or between a chain and a monomer. However there is a type of polymers known at cross-linked polymers which possess covalent bonds at sites other than the end of chains. The diagram below shows the schematic of a regular polymer and a cross linked polymer. Low amounts of crosslinking allow the polymer to have higher elasticity while larger levels of crosslinking provide higher structural rigidity.
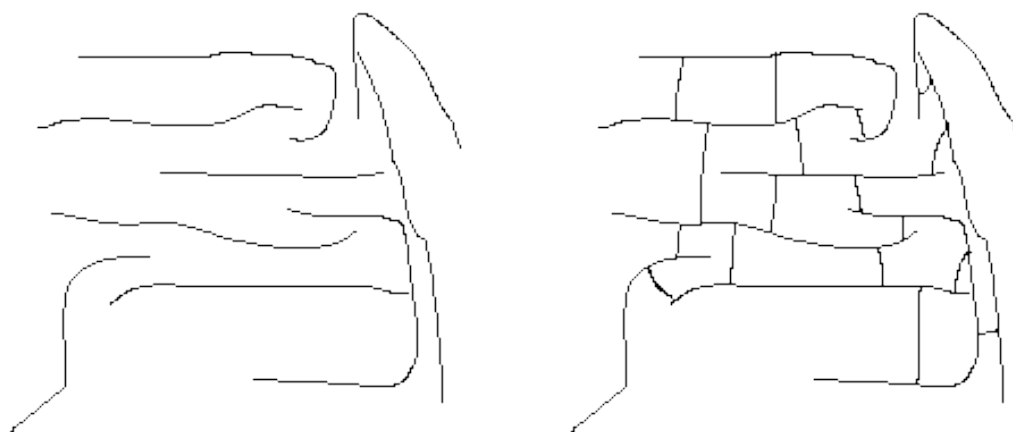

Figure 2 - Schematic of a regular polymer (left) and a cross-linked polymer (right)

Polymerization

Polymerization is the process by which monomers are chemically brought together to form polymers. The polymerization process can be divided into two main types of reactions, condensation and addition. Condensation polymers are also known as 'step growth polymers'. This method involves the simultaneous formation of several polymer chains at the same time, which may join together to form even larger chains. In addition to this, most condensation reactions also involve the release of small molecules such as water as byproducts. The condensation reaction of polyhexamethyleneadipamide is shown below. The polymer is more commonly known as nylon 66:
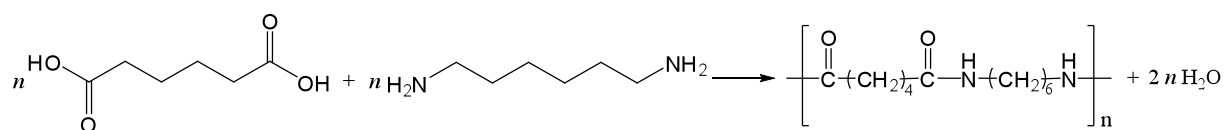
Figure 3 - Condensation reaction of nylon 66

On the other hand addition polymerization, which is also known as 'chain growth' polymerization does not produce any byproducts. Hence the full monomer is incorporated into the polymer chain. The mechanism for addition polymerization also differs from that of condensation in the sense that a single monomer is added sequentially to the end of a chain rather than having multiple chains which the join together as in condensation. An example of an addition polymer is polysterene:
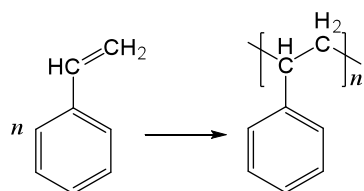
Figure 4 - Addition reaction of polysterene

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The diagram below is a schematic of the polymerization mechanisms of both condensation and addition reactions. As shown below the rate at which the monomers are consumed is much faster for condensation than for addition. Moreover in condensation reactions multiple chains are produced simultaneously rather than a single chain such as that of the addition mechanism. This results in the molecular mass of the polymer increasing much faster in condensation reactions than in addition reactions.

Figure 5 - Schematic of condensation (a) and addition polymerizations[3]

Stimuli Responsive Polymers

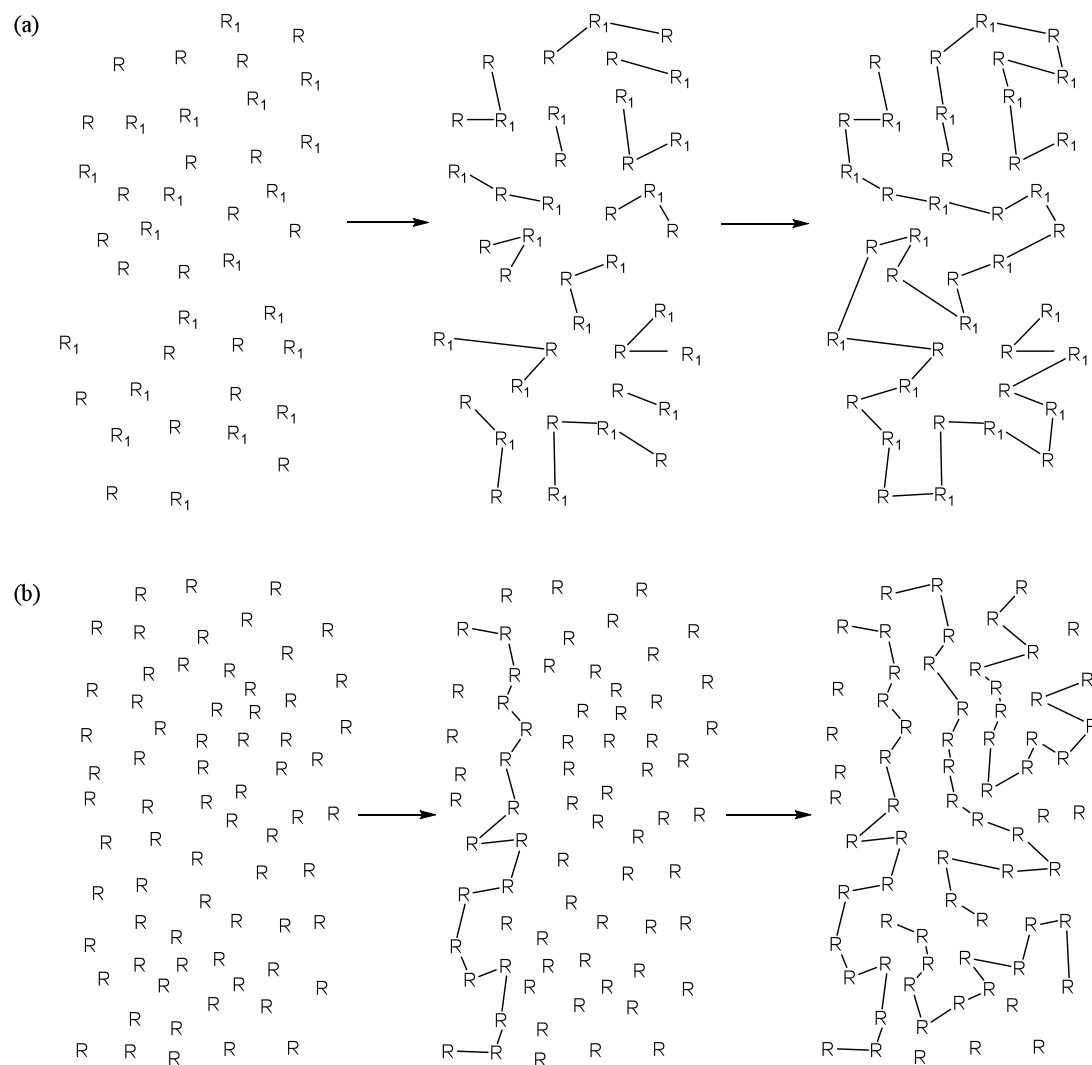Polymers are useful for many applications because of their ability to be molded into different shapes, their controlled flexibility and their strength. Another less commonly known property of certain polymers is their ability to respond to certain types of stimuli. The length, structure and functional groups are what may allow a polymer to respond in certain ways to certain stimuli. The name stimuli-responsive polymer is given to those materials which show dramatic property changes due to small changes in the environment. Researchers around the world have developed different polymers that respond to a variety of stimuli such as electric fields[6], magnetic fields[7], light[8], temperature[9] and pH change[10].

One of the first stimuli-responsive polymer materials was reported by Tanaka in 1982[11]. Tanaka reported that when an electric field was applied to a polycrylamide hydrogel the materials would either collapse or swell. The resulting difference in volume was as high a one hundred fold. These same gels showed similar responses to other stimuli such as pH and light. Materials such as this one could prove to be very useful in making functional nanodevices.

One type of stimuli response polymer which is directly related to this project is polymers which swell when exposed certain solvents. Similar to small molecules, polymers have the ability to interact strongly with certain solvents. Depending of the interactions some polymers can swell while others can contract when exposed to a solvent.

In a polymer–solvent system the solvent and polymer molecules may have certain affinity for each other. Whenever the affinity between the solvent and polymer molecules is high, then solvent molecules will cover the surface of the polymer. This will

in turn result in a larger spacing between polymers chains and hence increase the overall volume of the polymer. On the other hand if the affinity of the solvent for the polymer is low then surface of the polymer will not be covered with solvent molecules. It might even be the case that there is so little affinity for the solvent that polymer–polymer interactions are preferred. If this interaction is favored then the polymer chains will be packed together more closely and hence reduce the volume of the polymer structure.

The swelling or contracting behavior of polymers when exposed to different solvents can be described by the Flory – Higgings parameter[12]:

$$=\Delta \ \ P \ \ 2 \quad -\ln(1-x)+ \ \ 1- \ 1x \ \ 2$$

This equation provides a measure of the interactions between polymer and solvent. Whenever < 0.5 the interactions between solvent and polymer are preferred over polymer to polymer interactions, causing the polymer to expand. Whenever > 0.5 the polymer to polymer interactions are preferred causing the materials to contract.

One of the characteristics associated with cross-linked polymers is their tendency to swell whenever they are exposed to certain solvents. As shown by the diagram below, the presence of solvent induces swelling along the length of the polymer chain. This behavior was first reported by Flory and Rehney in 1943[13].
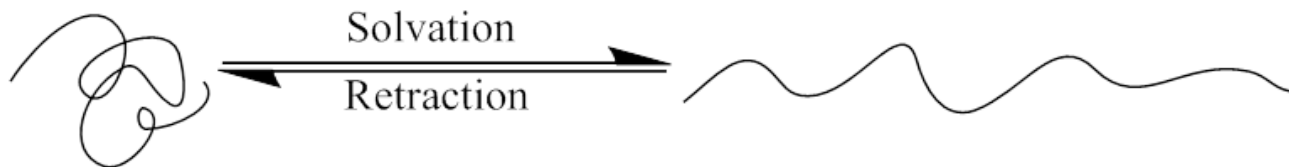
Figure 6 - Schematic of polymer swelling

Bilayer Polymeric Materials

As the name implies bilayer polymers refer to polymer materials which contain two distinct regions. These two regions can be two different polymers or one polymer with a metal layer. Following the same concept of Janus particles, the two regions tend to have different chemical compositions and hence different physical and chemical responses to stimuli. When placed in certain environments the different composition of the regions will introduce special actuation to the bilayer which could not happen with the individual components.

One example of these types of structures was prepared by Guan et al[7]. They fabricated a polymer–polymer bilayer of PMAA / PEGDMA by using soft lithography. When placed in water the flat bilayer structure would fold. Folding was caused by the different swelling ratios of the two polymers in the bilayer. Similar to a bimetallic strip, the monolayer with the higher swelling ratio would expand more than the other monolayer. This would in turn cause the first monolayer to curl around the less swelled layer and hence result in a curled structure. Guan et al were also able to control the extent of the folding by variations in the amount of each monolayer present in the bilayer structure. This type of material has potential applications in nanodevices. The ability of the wire

structures to curl when exposed to certain stimuli can be used to fuse different nanostructures together, in a sense working as a "nanostapler".

This project described herein presents the synthesis of micron sized polymer wires as well as the fabrication of bilayer structures through the use of metallic sputtering. Moreover the exposure of these structures to dichloromethane resulted in curling behavior. The nature of this behavior, including a proposed curling mechanism, is presented.

Synthetic Procedure

The reagents used for the synthesis of the micron sized polymer wires were,the imitator 2,2'-azobisisobutyronitrile (AIBN) which was purchased from either Sigma Aldrich or Fisher Scientific and recrystallized from methanol before being used. The monomer 4-ethoxy4'-(6-acryloyloxyhexyloxy) azobenzene and the cross-linker 4-4'-bis(6-hydroxyhexyloxy)-azobenzene were both synthesized and provided by Dr. Jianxia Zhang[14].

Polymerization reaction

Micron sized polymer wires were synthesized using a glass capillary array (GCA) template purchased from PHOTONIS Inc. The template used was 300 μm thick and had channels with a diameter of 5μm. The GCA template was attached to a glass slide using scotch tape. The monomer, cross-linker and initiator (AIBN) were combined in a 90:10:1 ratio. All three reagents were mixed thoroughly using an agate mortar and pestle. The resulting powder was then spread evenly on the GCA template and another glass slide was attached to the template in order to cover the reagents. The entire assembly was then placed in a flat bottomed flask. The flask was then attached to a Schlenk line in order to pull a vacuum on the flask. After a good vacuum was achieved the flask was frozen using liquid nitrogen. The flask was then refilled with nitrogen gas and placed in water to allow it to thaw. This process was repeated two more times and then the flask was heated on an oil bath overnight at 90°C. The assembly was the removed from the flat bottomed flask and the scotch tape was removed carefully. The GCA was the

placed in a dilute hydrofluoric acid solution (1%) in order to dissolve the template away and leave the wire structures only. The resulting polymer wires were then washed thoroughly with acetone and water.
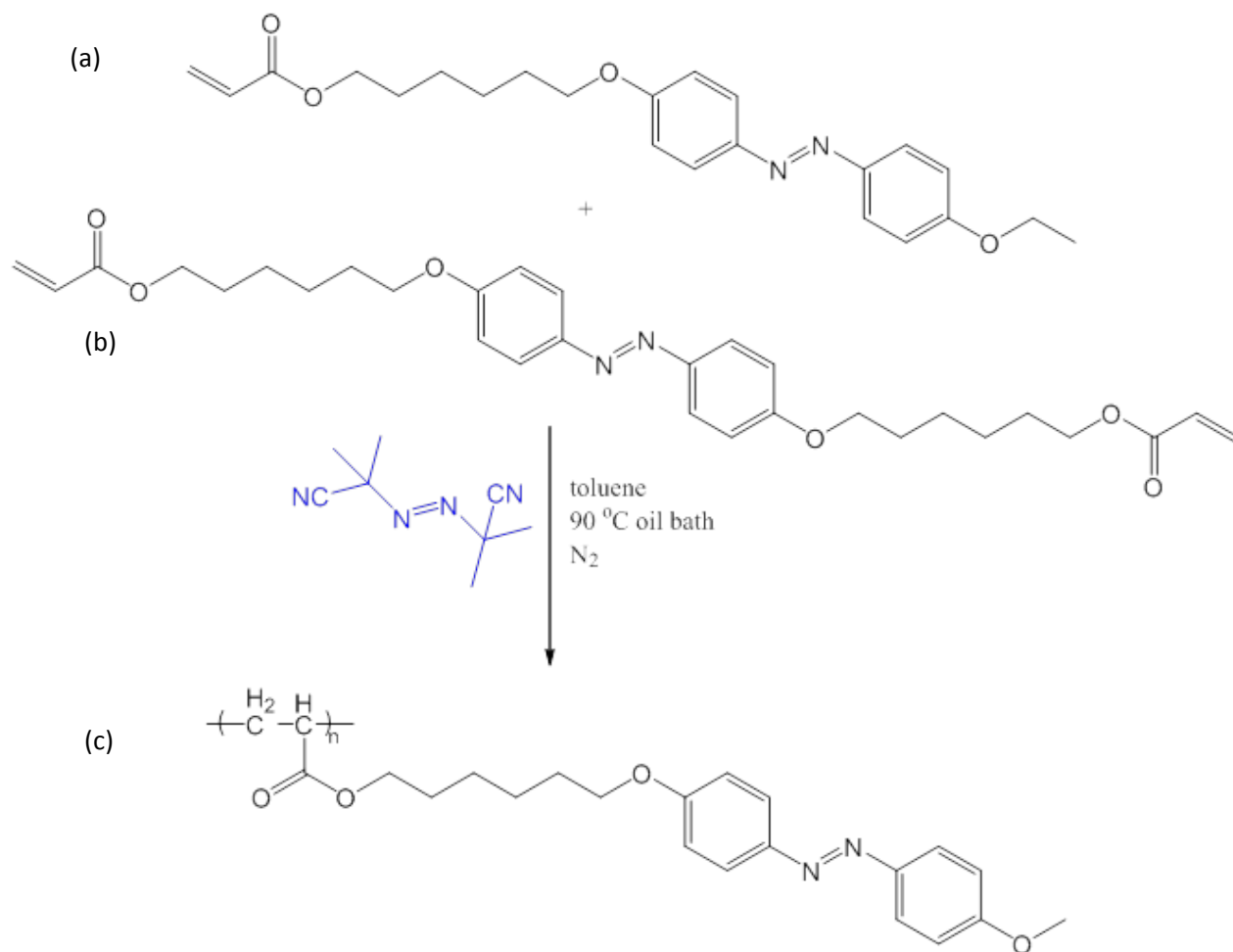
Sputtering of polymer wires

The washed polymer wires were dispersed on a clean silicon wafer. The wires were then sputtered with silver using a Denton Vacuum Desk II sputtering system using a

current of 40 mA. Different amounts of sputtering were done on different batches of wires in order to control the thickness of the metal monolayer.

Deformation Studies

After sputtering, some of the wires were transferred onto a clean Silicon wafer by gently rubbing the original wafer with a clean wafer. After being deposited on a clean silicon surface the wires were exposed to Dichloromethane (DCM). The behavior of the wires when exposed to DCM was observed and recorded. The exposure to DCM was done in numerous ways. In some experiments a whole batch of wires was exposed while other experiments only included a single wire. Moreover, direction of the solvent front was also controlled for some experiments.
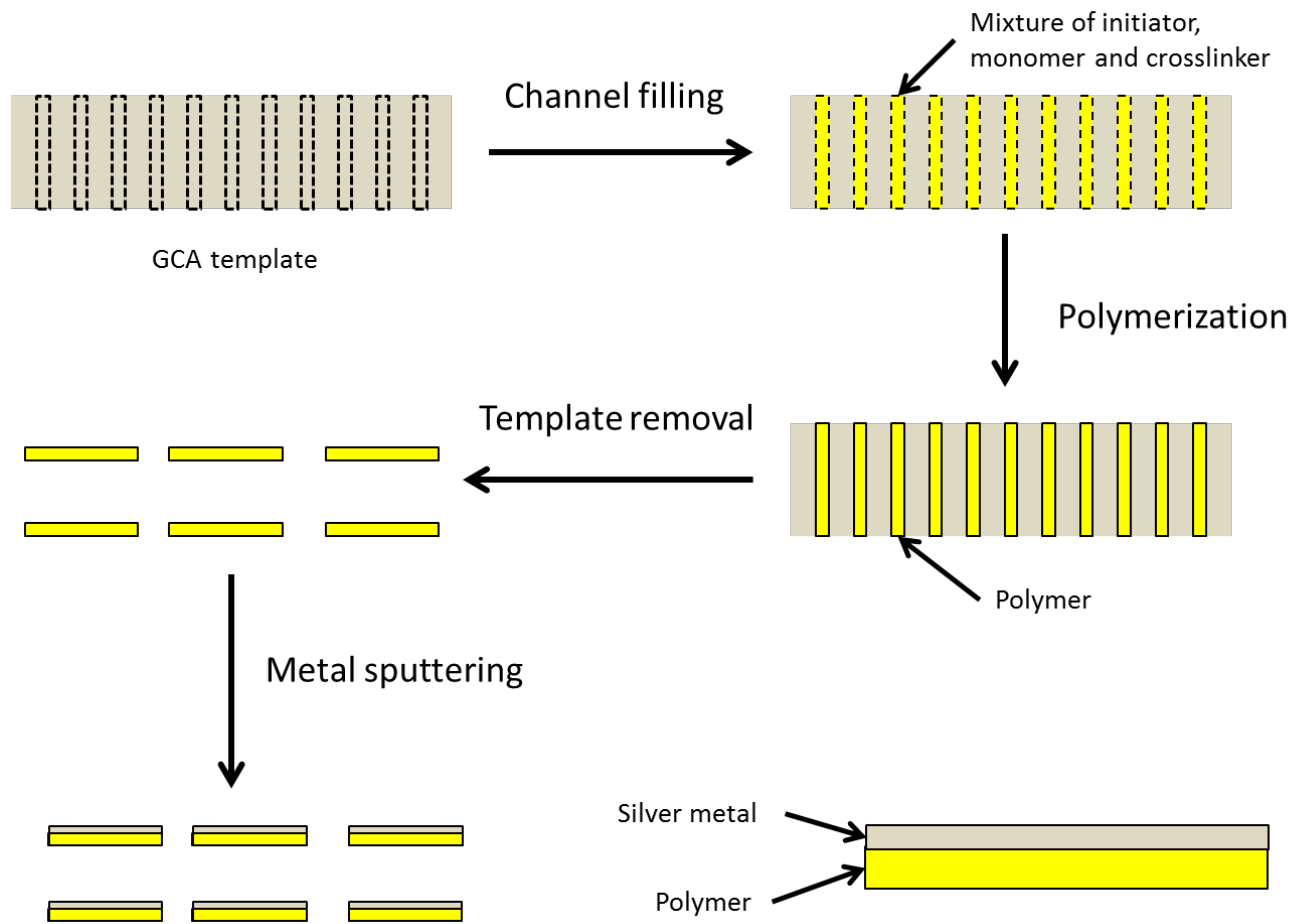
Figure 8 - Overall synthesis schematic. The empty GCA template was filled with the 3 component mixture. After polymerization the template was removed and the wires were sputtered

Previous Deformation Study

When exposed to DCM the wires curled into certain shapes. The deformation of a series of wires was investigated by Zhang et al. When wires with metallic layers of different thicknesses were exposed to DCM they behaved in different ways[14]. Wires with metallic monolayers ranging from 50 nm to 200 nm show instantaneous curling. Nonetheless the wires with metallic layers of less than 100 nm showed recovery to the original structure after the solvent was removed. On the other hand, wires sputtered with layers of 200 nm did not regain the original structure and hence remained curled

even after the solvent was removed. For metal layer thickness of 300 nm curling was stilled observed but it was much reduced. Finally metal monolayer of 350 nm showed no curling at all as shown in the table below.

Silver thickness (nm)	Deformation
0	Slight or no deformation
50	Instant deformation with immediate recovery
100	Instant deformation with slow recovery
200	Instant deformation with retention of curled structure
300	Slow deformation with retention of curled structure
>350	No deformation

The sequence of images below demonstrates the curling behavior of a single sputtered wire when DCM is applied. As can be seen the wires starts curling immediately after it contacts DCM. Very rapidly the wire changes from as straight wires to a complete circle.

Because the metallic monolayer of this wire is 200 nm, the curled structure remained even after the solvent was removed.

When this same experiment is done with a batch of wires rather than with single wires a similar behavior is observed. The image below shows a batch of polymer wires with 200

nm thicknesses after being exposed to DCM. As can be seen very few straight wires remain and most seem to have undergone some sort of deformation.
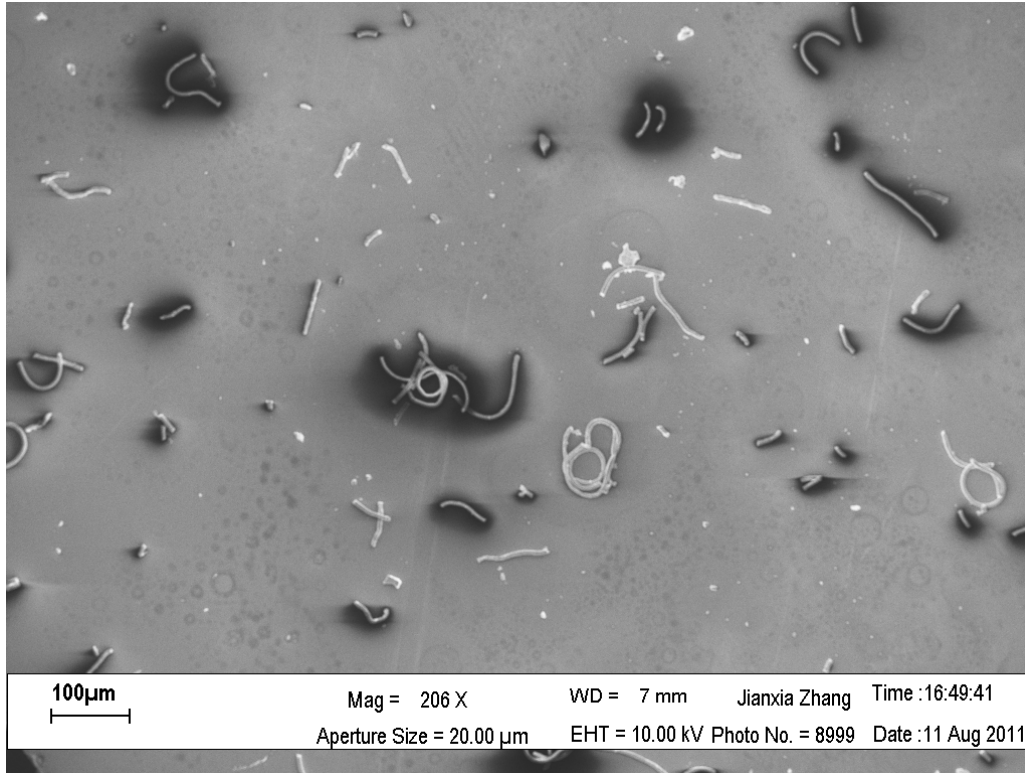

Figure 10 - Batch of sputtered wires after exposure to DCM[14]

It must be noted that the entire batch was sputtered the same amount and hence having different deformations within the same batch of wires is not intuitive. The wires that do curl into rings have varying curling orientations, with some left handed curls and some being right handed curls[14]. In addition to this, other shapes such as C shapes and S shapes are observed.
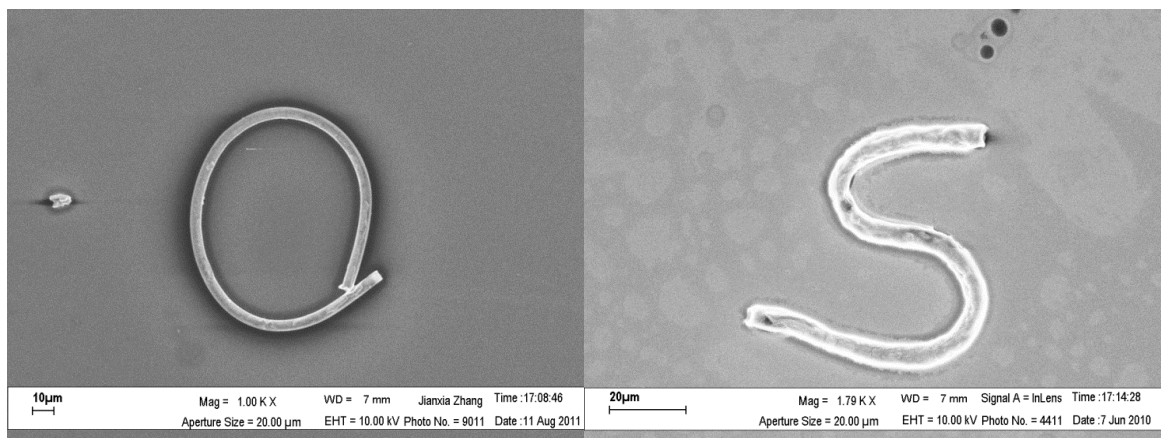
Figure 11 - Wire deformation into circular structure (left) and S shape (right)[14]

As can be seen the wires always seem to curl towards the sputtered side. Moreover the metallic film shows some fracturing caused by the curling. The SEM image below shows how the metallic monolayer resides in the inside part of the loop[14].

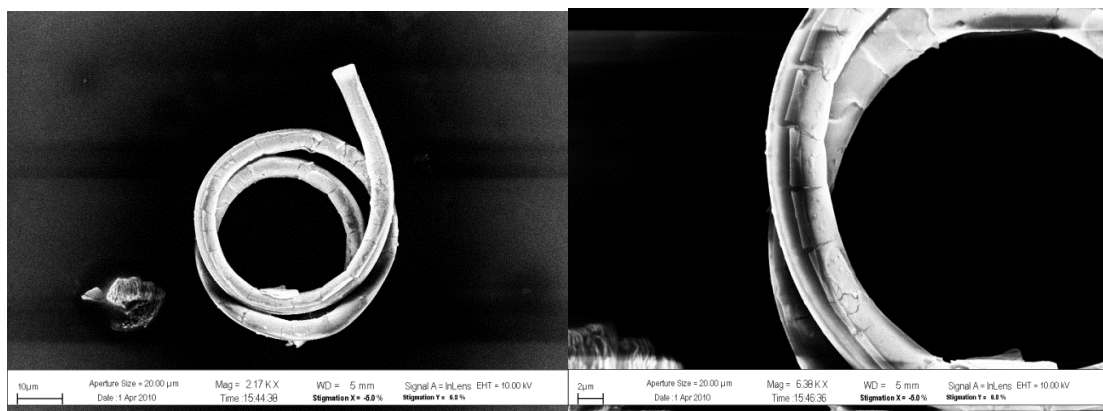Figure 12 - SEM image of curled wire (left). Zoom in of the same strcuture showing the metallic fragments on the inside of the loop[14]

Results

Synthesis of Polymer Wires

Micron sized polymer wires were readily prepared using GCA membranes as templates. The figures below show an empty GCA membrane (a) and a GCA membrane filled with polymer wires. After the glass membrane was removed the wires were dispersed on a

silicon wafer using a spatula or by rubbing the wires gently between two clean wafers.
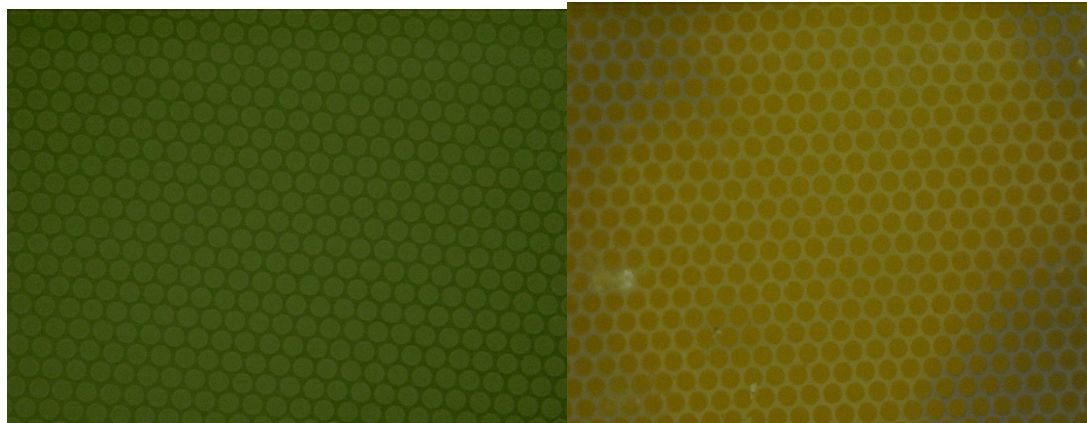

Figure 13 - Optical microscope image of empty GCA membrane (left) and GCA membrane after polymerization (right)

The image shows individual wires dispersed on a silicon wafer. Even though the GCA membrane was 300 μm thick not all of the wires were this long. Shorter wires were observed which likely broke off the original 300 μm wires.

Figure 14 - Dispersed polymer wires on clean wafer
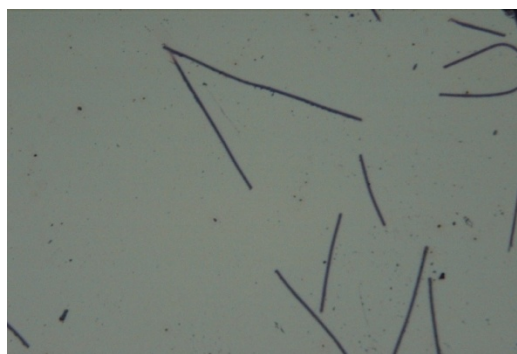
Inconsistencies in Curling Behavior

As shown in Figure 10 above, even when the polymer wires are sputtered in equal amounts there are inconsistencies in the curling behavior. In order to determine the frequency of these inconsistencies, individual wires were placed on a clean silicon wafer. In order to transfer individual wires to a clean wafer a capillary glass tube was

used. The wires were then exposed to drops of DCM and their deformation was observed and recorded.

As shown by the table below ten trials were done for this experiment. Wires of approximately the same size where chosen and the solvent was always introduced from the left side in order to reduce the variability in the experiment. In eight of the ten trials the wires curled in a circular shape. The wires only curled into C and S shapes once for each shape.

Even though similar looking wires were chosen for all trials of this experiment it must be noted that all wires have small defects. As seen on Figure 14 some of the wires have small bumps or breaks on them which could have some effect on the swollen structure.

Table 2 - Different deformations of polymer wires

Shape Observed	Occurrence
O	8
S	1
C	1

Solvent Direction

As shown above the direction of curling is directly dependent on the location of the metallic monolayer. An experiment was conducted in which single wires were exposed to DCM incoming from a variety of directions in order to determine the direction of the solvent had any influence on the deformation of the wires.

Individual wires were placed on a clean silicon wafer and observed through an optical microscope. DCM was introduced by placing a droplet near the wire. As the droplet expanded it reached the wire and resulted in deformation. The DCM droplet was placed in such way the solvent front would approach the wire in different directions as shown by the schematic below. The blue lines indicate the direction in which the solvent front is moving.
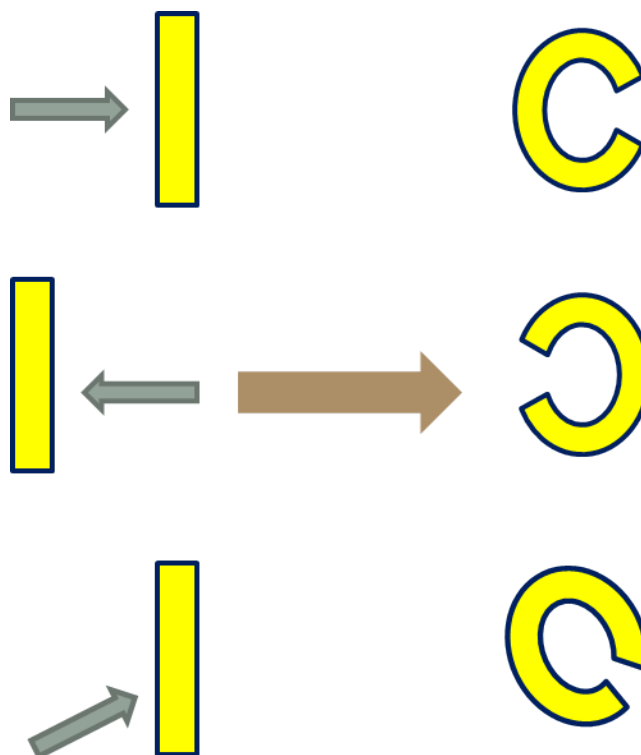

Figure 15 - Illustration of wire deformation based on solvent direction

The experiment was conducted six times. Regardless of the direction in which the solvent was introduced the wires would always curl away from the solvent direction as shown above.

Immobilization of a Single Polymer Wire

When attempting to control the direction in which the solvent front approached the wires it is important to acknowledge the possibility of the wire rotating when contacting the

solvent or even while curling. In order to eliminate this possibility an experiment was setup in which a single wire was immobilized onto a silicon wafer using wax.
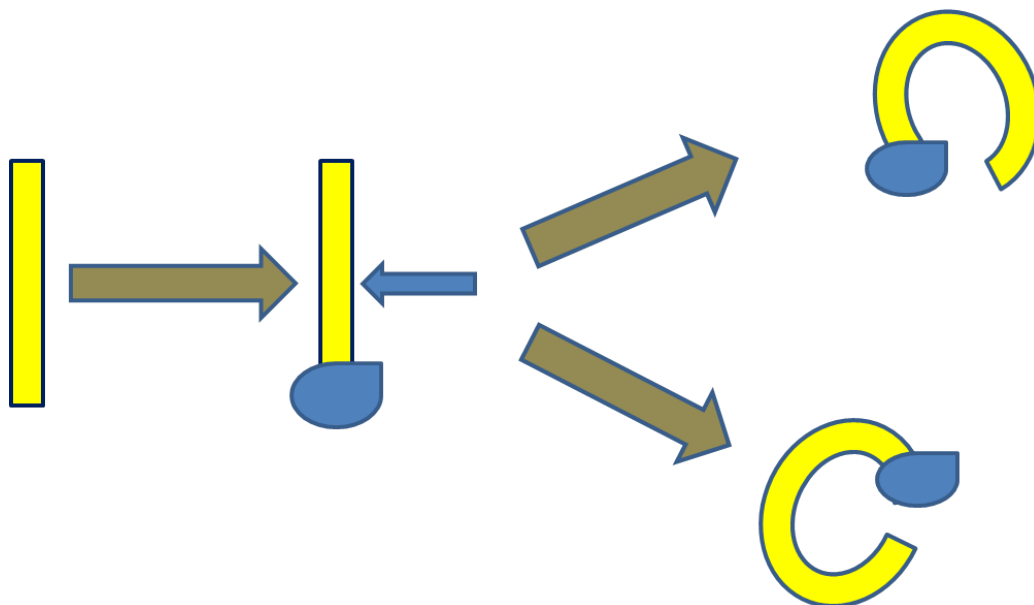

Figure 16 - Schematic of inmobilized wire curling.

As shown by the schematic above, when the wire was immobilized with wax (blue circle) the direction of curling was not dependent on the direction of the solvent (blue line). Unlike the first experiment, this experiment shows the wire curling towards and away from the solvent front. The experiment was repeated six times with the wire randomly curling both towards and away from the solvent.

Discussion

Micron sized polymer wires were synthesized using GCA membrane as a template. When the GCA template was dissolved away, the free wires were 5 μm in diameter but had varying lengths. The GCA template used had a uniform pore length of 300 μm. The shorter wires could have been caused by the pores in the GCA not being filled with enough starting materials. Another possible explanation is that the wires could have

fractured and broken into smaller pieces. This is especially likely to occur when the wires were transferred onto new wafers by sliding two wafers against each other.

When the sputtered wires were exposed to the solvent they would curl into particular shapes as shown in Figure 10. By looking at the SEM images (Figure 12) it can be observed that the metallic monolayer is located on the inside of the curled structures. The curling mechanism is analogous to what happens when a bimetallic strip is heated up. The polymer layer has the capacity to absorb solvent and swell. On the other hand the metallic layers are unaffected by the solvent and retains their regular shape. Because the two layers are attached the expanding polymer will curl over the rigid metallic layer. Hence in this system the polymer film is exerting a force to bend the metallic layer. The metallic layer on the other hand is merely opposing the force because of its inherent rigid nature (Figure 17)

However as can be observed from Figure 10 many of the wires did not curl into circles and often S and C shaped wires were observed after solvent exposure. The appearance of these unexpected shapes in the curled structures may indicate that perhaps there is something more than just the location of the metallic monolayers influencing the type of deformation observed.

By observing the behavior of ten individual wires it was determined that approximately 80% of the wires curl into circular shapes, while the remaining 20% curl into other shapes. This demonstrated that the circular shape is in fact the most frequent of all the curls as expected.
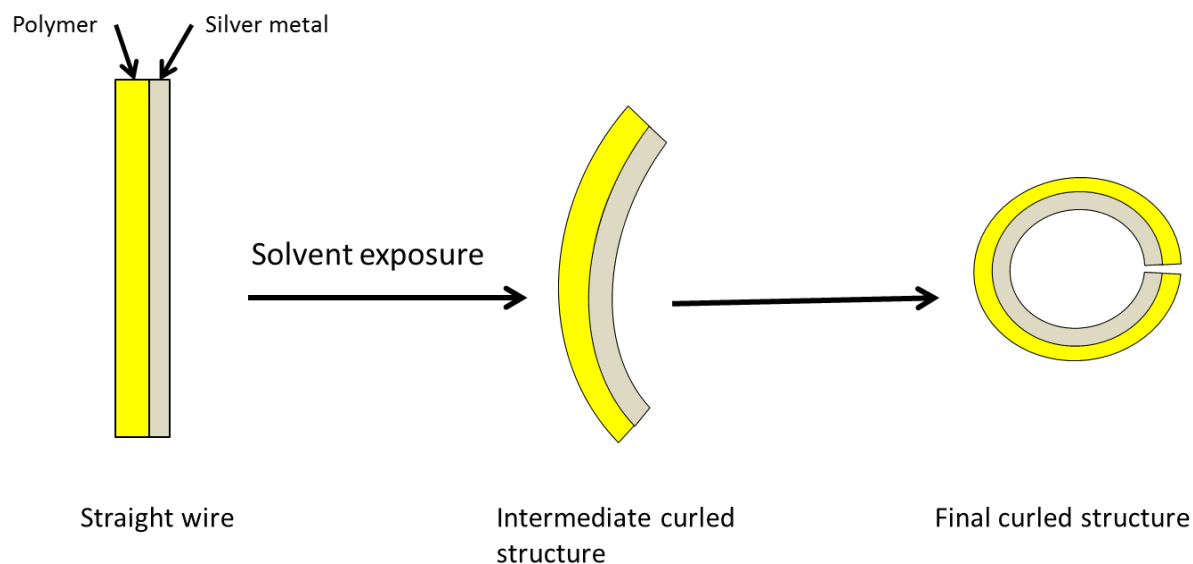
Figure 17 - Schematic of curling mechanism

The experiment attempting to use the direction of the solvent as a variable revealed that the wires would always curl away from the solvent regardless of the direction of it (figure 15). These results were somewhat contradicting to previous results which suggested the location of the metallic layer was responsible for the direction of the curvature. A possible explanation for this is that when contacting the solvent wires may be suspended in the solvent and rotate. In order to eliminate this possibility, individual wires where immobilized using wax. The result was that when solvent was introduced, the immobilized wires would curl both towards and away from the solvent. This result suggests that the direction of the solvent does not have any influence on the direction of curling, which is dictated by the location of the metallic layer. Moreover this also suggests that when the wires are not immobilized they somehow rotate and the curl away from the solvent. The reason why free wires rotate and then curl rather than just curl immediately is unclear.

The experiments conducted demonstrate that solvent is not a factor which affects the curled structure of the wires. However this does not explain why some of the wires curl differently than others. A possible explanation for this is that when mechanically transferring wires, by rubbing two wafers together, the wires may twist before being exposed to the solvent. When exposed to DCM the polymer would again swell around the metallic layer but because of the twisting, this time it would produce an S shape. Nonetheless other possibilities for the abnormalities in the swollen structures could be attributed to uneven sputtering and non-homogenous polymer composition.

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APPROVAL SHEET

This is to certify that _Juan Francisco Callejas_ has successfully completed

his Senior Honors Thesis, entitled:

Induced Asymmetric Deformation of Silver Coated Micron-Sized Wires

_____ Director of Thesis
John B. Wiley

_____ for the Department
Gabriel Caruntu

_____ for the University
Carl D. Malmgren   Honors Program

May 3, 2012
Date