Project Number: BE07

Fabrication Methods for the Characterization of Nanorods Using Multilayer Polymer Thin Films

A Major Qualifying Project Report:

Submitted to the Faculty

Of the

WORCESTER POLYTECHNIC INSTITUTE

In partial fulfillment of the requirements for the

Degree of Bachelor of Science

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Acknowledgements

The authors are extremely grateful to their advisor, Professor Jiang for all her help and guidance. We would also like to thank Shelley Dougherty for assisting us in the development of our procedures and assisting us with SEM and TEM imaging and analysis. We extend thanks to the Biomedical Department of Worcester Polytechnic Institute and Lisa Wall for sponsoring our project and aiding in the ordering of all our needed supplies, respectively.

Abstract

Nanoporous templates have seen increased use as a method of creating controlled size nanotubes and nanorods. Currently, the method has focused on the creation of nanomaterials composed of singular polymers or polymer blends. Our study focuses on creating nanomaterials composed of alternating sections of various polymers in a highly controlled manner. The heterostructured, one dimensional polymer nanomaterials may serve for various uses, including biosensors, drug delivery, and biomimetic applications.

1. Introduction

The technique for fabrication of polymer nanotubes by template wetting provides narrow size distribution and highly controllable orientation of the one dimensional (1D) nanomaterial. When put in contact with a nanoporous template, polymer melts or solutions are pulled into the nanoporous channels due to capillary forces or surface forces and form nanorods or nanotubes. This occurs due to the energy difference between the high energy alumina template and the low energy polymer melts provides an interfacial driving force that promotes the template wetting process. This method is applicable to single polymer, polymer blends, or multiple component solutions [1]. The template-based synthesis of nanomaterials has numerous potential applications in various areas such as biomedical sciences, electrochemistry, and drug delivery [2]. Currently, the production of heterostructured 1D polymer nanomaterials using a single template has not been reported. Our method of controlled wetting of nanoporous templates with alternating polymer layers provides a novel approach that may expand the available applications of nanomaterials.

2. Materials

Polystyrene (PS), polymethylmethacrylate (PMMA), and polyvinyl chloride (PVC) were dissolved in various solvents. PS and PMMA were dissolved in Toluene and PVC was dissolved in tetrahydrofuran (THF). Glass slides were spin coated with the polymer solutions. Porous anodized alumina oxide (AAO) was used as the template to create the nanorods. Hot plates were used to control the temperature.

3. Methods

Polymer solutions of various concentrations (weight percentage); such as 5%, 10%, 15% and 20%, were employed to control the thickness of the film on the glass slides. PS and PMMA were dissolved in Toluene and PVC was dissolved in THF. All solutions were mixed using a stir bar until completely dissolved. Combinations of different speeds and concentrations were explored to determine reliable control over thickness of polymer coatings on the slides. 100 mL of solution was placed on each glass slide using a pipette for spin coating. The 10% PS solution was spun at 4000 RPM for 60 seconds while the 10% PMMA solution was spun at 3000 RPM for 60 seconds. PS and PMMA alternating layers were coated on glass slides until an approximate total thickness of 1μm has been reached. AAO templates were then placed on top of the polymer thin film. The polymers were heated up to 150°C by hot plate. After polymer nanotube/nanorod fabrication, AAO templates were removed by dissolving in NaOH for an extended time. The polymer nanorod samples were cleaned and purified by centrifuge. Finally, scanning electron microscope (SEM) and transmission electron microscope (TEM) were employed to analyze the samples.

4. Results and Discussion

SEM photographs were able to show that the templates did in fact produce cylindrical nanostructures on our glass slides. The ends of nanorods are in the shape of dimples due to the capillary effect. So SEM top view images of nanorods and nanotubes look very similar.

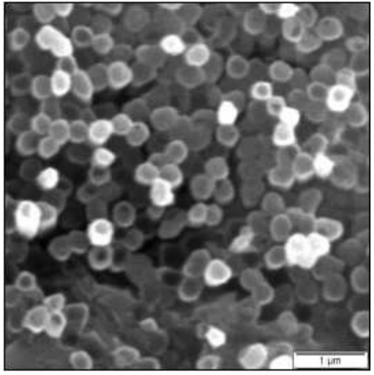

Figure 1 *SEM picture of the top view of several nanorods clustered together after the removal of the AAO template.*

A TEM close up of the end of an individual nanorod as seen in Figure 2 illustrates the dimpled shape.

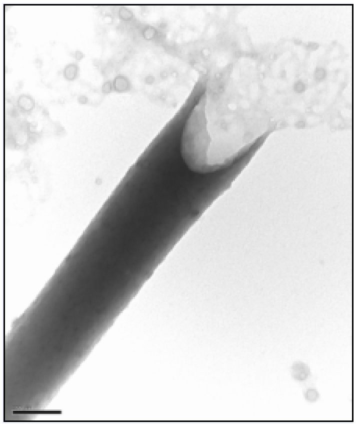

Figure 2 *A TEM picture of the side of a nanorod illustrates the dimple effect. Shown against a scale of 100 nanometers.*

Figure 3 demonstrates the successful fabrication of a polymer nanorod with alternating layers of polystyrene (PS) and polymethylmethacrylate (PMMA). The PS segment is dark because PS was selectively dyed.

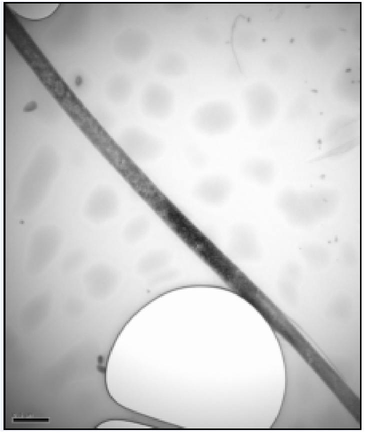

Figure 3 *TEM picture of a PS and PMMA layered nanorod.*

Our results prove that it is possible to create alternating sections of polymers within a single nanorod using only one template. The research and testing are currently ongoing in order to determine the amount of control that can be achieved when creating alternating layers gain better control over the fabrication process. For example, we believe that the length of each polymer segment in the nanorod can be controlled by controlling the amount polymer melts/solutions on the glass slide but this is not yet been tested.

5. Conclusion

Our method consistently creates heterostructured polymer nanorods with alternating sections which can be incorporated with different functionalities to realize novel properties. The process is reproducible and can be readily scaled up for commercialization. The nanorods produced by this method can be used in various applications including biomedical sensing, drug delivery, and electrochemistry applications.

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3 Problem Statement

The fabrication and characterization of heterostructure nanorods has received increased study due to the unique properties of the one-dimensional structures created. This increased study has fueled a need for inexpensive, reproducible, and easily scalable production. By characterizing and understanding these structures, their unique properties can be better utilized. The process of template wetting is an inexpensive, scalable, and customizable process that can fabricate nanostructures for a wide array of polymers. To investigate the characteristics of heterostructure nanorods, Polystyrene (PS) and Poly(methyl methacrylate) (PMMA), whose characteristics are seen in Table 1, are selected as the model materials. Polyvinyl chloride (PVC) was also studied, but was deemed unsuitable for further investigation towards the fabrication of polymer nanorods in this project due to difficulties in processing.

Table 1 - Properties of Polystyrene and Poly (methyl methacrylate) (Bloch, 2005)

Polymers	**M_w**	**T_g (approx.)**
PS	230,000	100°C
PMMA	120,000	100°C

The characteristics of heterostructure nanorods will be investigated by controlling polymer thin film thicknesses, weight percentage of solution, wetting time, and wetting temperature.

4 Introduction

The human population is growing due to advances in medicine increasing the average life expectancy, with this increase in life expectancy people expect their quality of living to increase in their final years.

In 1960, the first pacemaker was implanted into a human being. For this to be done a device needed to be made that contained a battery, was biologically inert and could respond to a change in heart rhythm with a pulse of energy. Today not only has the size of the device, as a whole, been reduced but there are many added features. Pacemakers now carry a small hard drive to store data about the patient's heart rate and can synchronize the beats of multiple chambers of the heart. While the pacemaker is an example of the use of micro technology forging advances in medicine, today there is much promise in the research and development of nanotechnology. There are currently many devices in the medical field which are large in size and require a patient to remain in a hospital for the duration of their use. The introduction of nanotechnology may one day be able to reduce the size of machines, such as a dialysis machine, by such an extreme amount that the devices will actually be able to be implanted into the body much like a pacemaker. By aiming to control processes on increasingly smaller scales, researchers hope to be able to control individual atoms, utilize them for a function, and then visualize the result.

The introduction of nanotechnology has introduced both risk and reward in the form of stronger, more applicable materials, but the unknown long-term effects of their use. The increased control over nanosized materials has allowed a new field of materials with unique characteristics in relation to their bulk counterparts. Increased study into nanotechnology has shown little development in the fabrication of heterostructure polymer nanorods. To study the properties of heterostructure polymer nanorods, polystyrene and polymethylmethacrylate were used to create segmented nanorods in our project.

The study of the fabrication and characterization of polystyrene and polymethylmethacrylate rods was performed due to the lack of greater knowledge in the field. By knowing the various parameters surrounding the creation of heterostructure nanorods it is possible to create multi-layer polymer specimens with sections of varying controlled lengths. This would allow the combination of properties of two or more polymers into a single rod given the knowledge of several factors: the rod length produced at a given temperature, a given time, and a known polymer thickness. By controlling this process with simple polymers we hope to create a template that can be used for combinations of biomedical polymers that could be used for drug delivery, biomaterials, and other applications.

By modeling this process with two common polymers, polystyrene and polymethylmethacrylate, the foundation of this process will be explored and characterized. To understand how this is done, it is necessary to understand the importance of nanotechnology and current methods for the creation of nanomaterials. Background to the problem will be presented so that the problem may be better understood. Current fabrication methods and techniques will as well as the specific aims and hypotheses of our project will be discussed. The methods used to fabricate heterostructure polymer nanorods will be presented and the results of our work will be analyzed. Lastly, future reccomendations will be given for further work in the area.

5 Literature Review

5.1 Importance of Nanotechnology

In the fiscal year 2005, more than $1 billion was spent on nanotechnology by federal agencies. Private investments exceeded $5 billion in the United States alone with global expenditures reaching even higher. Nanotechnology has blended engineering, chemistry, biology, and medicine in unexpected ways. The field has become one of the most prominent interdisciplinary fields with the Bush Administration's National Nanotechnology Initiative, a multi-agency program slated to build, characterize, and understand nano-scale devices. On a national scale, the NSF will receive $305 million in 2005, the Department of Defense $276 million, as well as the National Institute of Health receiving $89 million (Vastag, 2004). These institutions represent varied interests but upon reflection show great growth in the field of nanotechnology. Nanotechnology has already seen applications in medicine with many drugs in phase III trials. For example, Abraxane, manufactured by American Pharmaceutical Partners Inc. is a treatment for metastatic breast cancer. Through the application of nanotechnology, they have developed nanoparticles coated with paclitaxel and by dropping the drugs directly into cancer cells the drug could potentially eliminate the use of toxic solvents that limit drug dosage (Vastag, 2004). The growth of the industry however, also brings concern over the harmfulness of products.

Nanotechnology has encompassed a new, sophisticated way of creating materials, which often have adopted unique characteristics separate from bulk material. In creating new materials it is important to assess the risks that are presented as new challenges emerge in ensuring safe nanomaterials. However, despite these inherent risks, nanotechnology has bloomed into the next industrial revolution with researchers discussing applications in industry such as stronger materials and better batteries in the short-term, and potential applications such as cancer treatments, greatly improved sensors and detection, and even life-mimicking devices in the future. This rapid progress brings with it hope of a better quality of life, however, the past has shown that technological advances can bring large impacts on society. The perceived or real risk can become a significant factor the development of nanotechnology.

Perhaps the best known nanomaterial is the single wall carbon nanotube (SWCNT) produced by Iijima in 1991 (Huczko, 2000). Composed of a single sheet of graphite rolled into a tube of approximately 1.5nm it exhibited high strength-to-weight ratio, thermal conductivity, electrically conductivity, and could even become an insulator if the atomic configuration was altered. This discovery has spurred interest in biological fields with efforts towards replicating biological functions, in medicine with targeted drugs, and even the creation of a nanocar at Rice University which demonstrated directional motion on a surface (Huczko, 2000). These achievements have proven how diverse a concept nanotechnology is, representing more a method of creation, than a discrete technology. The science of nanotechnology has demonstrated three major concepts—control, utilization, and visualization. These terms include the ability to place quantities of material where desired, the ability to use nanotechnology for a practical purpose, and the ability to detect where the material is placed and configured at scale. While these materials present great promise, it is unavoidable that there is a level of uncertainty surrounding the potential risks and the long-term effects will not be known unless addressed systematically.

5.2 Nanostructures

Nanostructures, often regarded as structures on a scale of 1 to 100 nm have created growing interests in their applications and properties. The superior properties in relation to their bulk counterparts have made the miniscule structures increasingly desired as stronger and more versatile uses are being found for their application. The advancement of modern science necessitates the increasing control over smaller and smaller structures in order to increase performance and various other parameters. Recently, one-dimensional nanostructures such as rods and tubes have become the focus of intense research due to their unique applications in the fabrication of nanoscale devices. These devices not only provide good systems to test the dependence of mechanical, electrical, and thermal properties based on size, but provide increased characteristics in these properties as well. The strategies for achieving one dimensional structure vary; six methods are shown below as presented by (Xia, 2003).

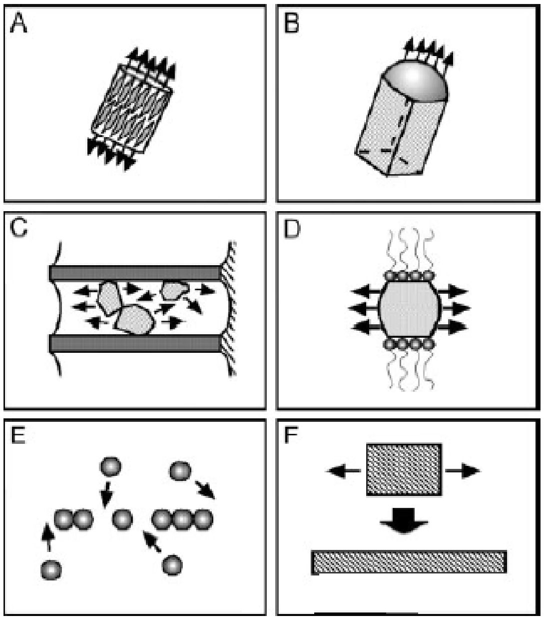

Figure 4 - Schematic illustrations of six different strategies that have been demonstrated for achieving ID growth

5.3 Summary of Methods and Materials

Nanotube applications spread numerous disciplines; however, they have spurred great interest in the biomedical field. Biodegradable polymers have been used as scaffolding materials extensively in the field to assist in regeneration of new tissues. Able to mimic the necessary characteristics including a three-dimensional structure, high porosity, and a suitable surface structure for cell attachment, proliferation, and differentiation, nanomaterials have found great promise as scaffolds for tissue engineering. A study by (Chen & Ma, 2004) developed a novel method for creating nano-fibrous poly (L-lactic acid) scaffolds with interconnected spherical macro pores. The aim was to develop a scaffold that mimicked the natural extracellular matrix, exhibiting behavior including suitable surface characteristics, porous network to allow the transport of soluble molecules and nutrients and a three-dimensional template to allow the tissue to hit its final shape. Due to the existence of collagen (I) fibers on the nano-meter-scale, scaffolding could be created to mimic these dimensions to provide superior scaffolds for tissue engineering. Paraffin microspheres were used as a porogen in the fabrication of the scaffolds, which, after several treatments in various solutions and at various temperatures they were successful in creating a number of nano-fibrous matrices with macroporous structures. The matrices were created with varying polymer concentrations and pore sizes which resulted in various density and porosity measurements. This example shows the viability of current technologies and their applications to the biomedical field. In the discussion of the experiment, the authors discuss the results of initial studies which show significantly superior results with the nano-fibrous pore walls compared to micrometer sized scaffolds. Nanomaterials have found other uses in the biomedical field as well, not limited simply to the creation of scaffolds in the assistance of tissue regeneration, but the refinement of drug and medication delivery.

Bi-directional wetting of porous alumina template has been carried out previously by ((Kriha, 2007). The templates were first wetted with PS-*b*-PMMA diblock copolymer and heated above the glass transition temperature. After the template was wetted with this polymer it was etched from the opposite side of the template and was wetted with PVC. The bidirectional wetting of the template resulted in a polymer that was of half length PS-*b*-PMMA and half length PVC and had varied optical, mechanical, thermal, and electrical properties along the long axis of the polymer. Through similar application single polymer can be used to wet a template and create various lengths of polymer to give each customizable polymer blend unique characteristics.

The dental industry faces an increase in prevalence of periodontal destruction with increasing age. The treatment of periodontal defects with an agent has received increased focus from materials scientists due to the economic and scientific significance. In the pharmaceutical domain, nanoparticles have become the subject of intense research and development due to the development of biosensors based on optical properties of colloidal gold nanocrystals to be used in medical imaging. By synthesizing metallic and polymeric nanoparticles it is possible to assist in the timely and accurate release of drugs by creation of tailor-designed structures. This development requires the interdisciplinary cooperation of material scientists, biologists, and chemists to assist in the characterization of the materials and their applications.

The driving force behind nanomaterials properties is the scale of design resulting in significant surface effects, quantum effects, and size effects. Traditional materials are found to have worse performance when compared to nanomaterials, which exhibit enhanced toughness, stiffness, heat resistance, as well as chemical, optical, and magnetic properties which differ from bulk materials. The creation of nanoparticles can be controlled to change their surface, structure, or shape. A method developed by Decher introduced the construction of multilayer assemblies based on layer-by-layer adsorption. As seen below, the creation of hybrid polymer/inorganic nanocomposites can be accomplished by hollowing out inorganic silica by electrostatic layer-by-layer assembly.

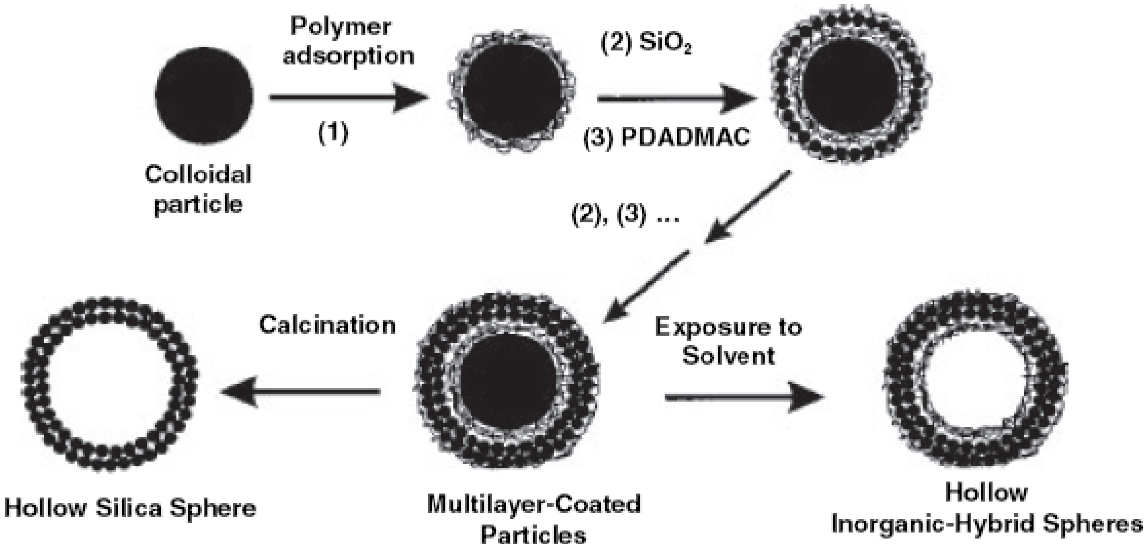

Figure 5 - Illustration of procedures for preparing inorganic and hybrid hollow spheres. The scheme is shown for polystyrene latex particles.

This procedure is readily controlled by varying the number of deposition cycles and the size and shape produced are determined by the dimensions of the template employed. While the creation of nanosphere is generally easier than nanorods, nanofibers, and nanotubes, this does not eliminate the latter from being developed for a host of biomedical and biotechnological applications.

Nanorods have been used in dentistry by (Chen & Ma, 2004) to mimic the biomineralization process of dental enamel by using highly organized nanorod-like calcium hydroxyapatite crystals. Further studies of nanotubes by Kolhi & Martin; have indicated that nanotube structures offer many advantages over spherical nanoparticles for many applications.

Nanotubes can be created by various methods, some examples of which are, organosilicon polymer nanotubes, self-assembling lipid microtubes, template-synthesized nanotubes, and peptide nanotubes. The large volume of these tubes serves well for biotechnological applications as drug delivery devices. The open ends of the nanotubes allow for accessibility and the tubes exhibit the ability to differentially functionalize the inner and outer surfaces. TiO_2 nanotubes have been processed into arrays of vertically aligned tubes which during *in vitro* immersion in a simulated body fluid were shown to have nucleation and growth. The success of prior experiments in creating viable nanomaterials and nanotubes for both industrial and scientific needs has shown the necessity to pursue further development of new nanomaterials.

The template synthesis of nanomaterials can be used to create nanotubules and nanorods of various materials. It is possible to deposit polymers, metals, carbons, and other materials in the pores of a template in the creation of rods and tubes. The creation of tubes versus rods can be controlled by changing the polymerization time. For some polymers, e.g. polypyrrole, the tubules will form solid fibrils, while others e.g. polyaniline will never become rods even at very long polymerization times. Rods and tubes with lengths equivalent to the pore depth and diameters larger than the nominal diameter of the template can be created by the wetting method. Electroless deposition involves the wetting of an alumina membrane with a solution of the desired polymer. After heating for a prolonged period of time, the alumina membrane is dissolved with NaOH and the tubules that filled the pores in the template remain.

The method chosen to be used was the creation of polymer nanotubes by wetting of ordered porous templates. When a polymer solution is placed on a high surface energy substrate, it will spread thin to form a thin film. When this thin surface film is brought into contact with a porous template, a similar phenomenon will occur. The polymer melt will cover the pore walls during the initial stages of wetting. Due to the cohesive driving forces being comparably stronger than the adhesive forces, the polymer melt will wet the wall first and completely fill the pore on a later timescale. The complete filling can be prevented by solvent evaporation in the case of solutions. If the template is ordered and of monodisperse size distribution, the polymer nanotubes can be preserved in the same form when the template is removed. Due to the versatility of the process, functionalized nanotubes of various forms can be created with relative ease. When the template and polymer melt are placed at temperatures well above the glass-transition temperature, to ensure complete melting in the case of amorphous polymers, the liquid polymer will show complete wetting on a short timescale. The method can also be extended to form composite nanotubes consisting of a polymer and a metallic element. The customizability of this method provides for functionalized tubes for a broad range of nanoscale applications.

6 Project Approach

The aim of the project was the fabrication of heterostructure polymer nanorods by template assisted wetting as shown in the methodology in Figure 6. To achieve this it was necessary to first fabricate multi-layer polymer thin films by spin coating glass cover slides with various concentration solutions of PS and PMMA. The polymer thin films were then characterized by UV-vis spectroscopy to determine the thickness of the layers created. After characterization, heterostructure polymer nanorods were fabricated by template assisted wetting as seen in Figure 7. These nanostructures were then analyzed using SEM and TEM to verify the successful fabrication of heterostructure polymer nanorods. These steps were deemed necessary to fulfill our specific aims and confirm our hypotheses below.

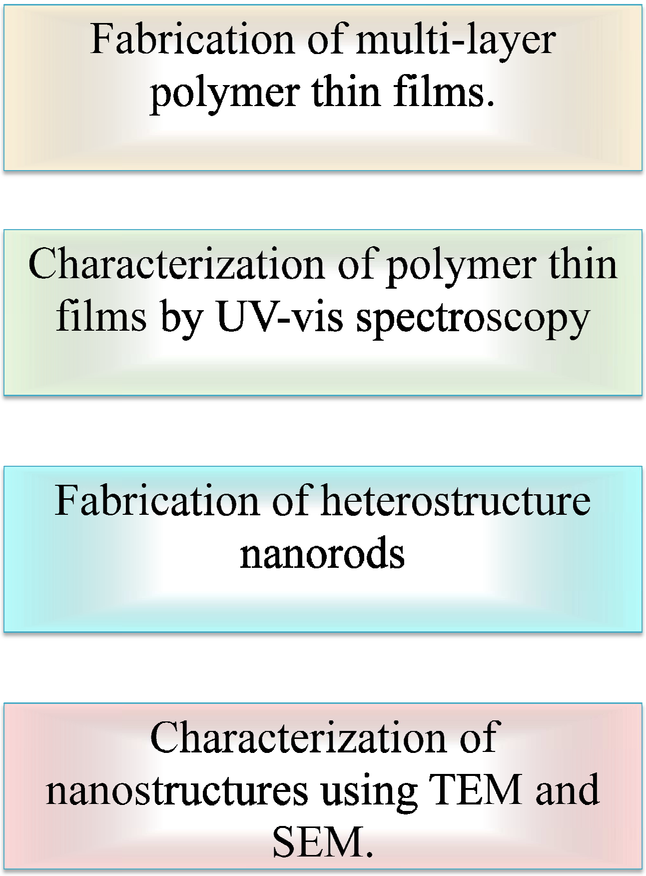

Figure 6 - Methodolgy flow chart depicting major process steps involved.

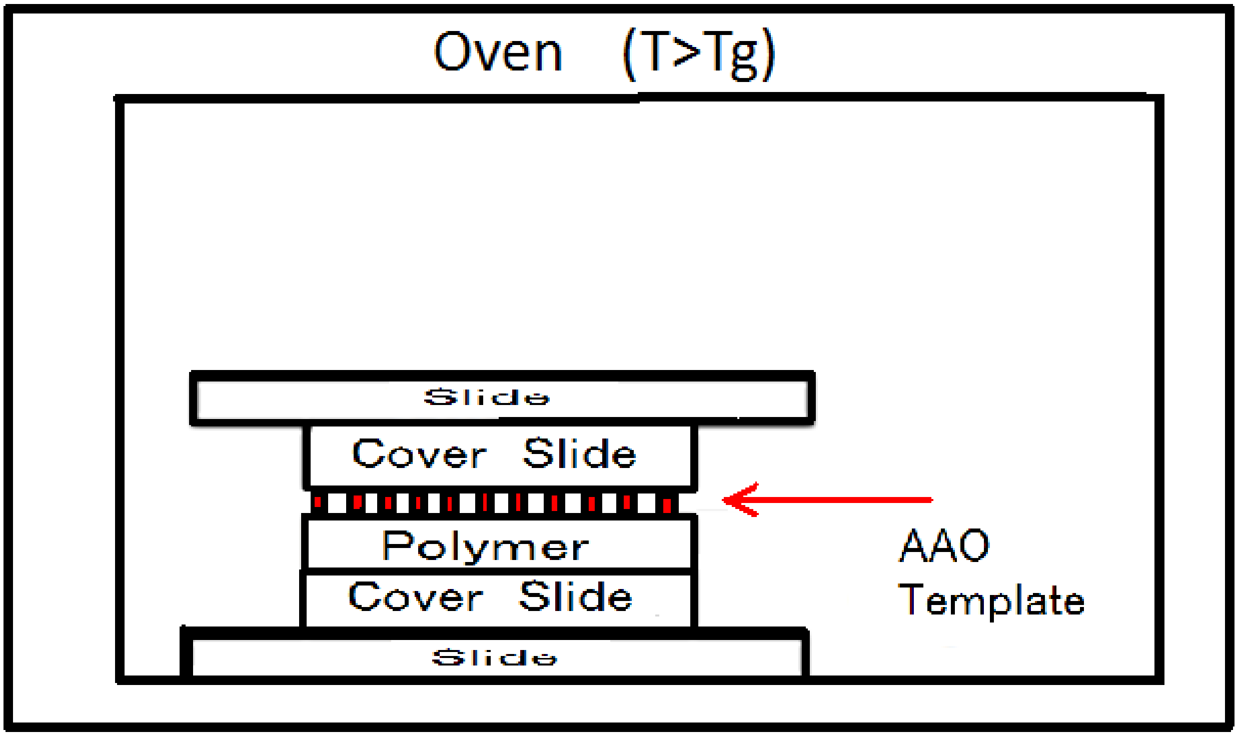

Figure 7 - Schematic of the template assisted wetting process.

Hypothesis 1: The application of different polymer layers will produce a single rod composed of the various polymers in sequence. Since the process of polymer wetting of porous templates has been proven successful with a single polymer as well as with the addition of metallic elements, it is logical that the inclusion of various polymers should exhibit similar properties to that of standalone polymers. The glass transition temperatures must be comparable due to the possibility of amorphous polymers. If the glass transition temperatures of the polymers are too varied, then the melting temperature of one polymer may occur at the same temperature as the glass transition temperature of a different polymer resulting in uneven wetting and a mixing of polymers. An undesired mixing of polymers will not allow controlled segments and heterostructure nanorods.

Specific Aim 1: Conduct various experiments with varying thicknesses of polymer layers. Heat polymers at temperatures well above both glass transition temperatures. Observe the results in an SEM to confirm the creation of a singular rod composed of various polymer components.

Hypothesis 2: Varying polymer thickness layers created by varying polymer solution weight percentages will create varying length nanorods under constant conditions. The wetting of the polymer occurs at temperatures above the glass transition temperature. By varying the time and temperature it is possible to control the amount of wetting in the porous template. This would allow the controlled production of known length nanorods.

Specific Aim 2: Conduct various experiments with various thicknesses of polymer layers. These layers would be created by spin coating glass slides at various RPMs with increasing weight percentage solutions of polymer. Multiple coatings could be performed to create thicker films. Film thickness of a single layer will be determined as a baseline and graphs developed to predict film thicknesses at higher RPMs. Under constant conditions various thickness polymer films will be heated above the glass transition temperature and the lengths of the rods created will be compared.

Hypothesis 3: The combination of various polymers into a heterostructure nanorod will create a segmented nanostructure with identifiable segments. The wetting and subsequent heating of the template will allow a controlled process with identifiable results.

Specific Aim 3: Conduct various experiments with different thickness polymer layers and subsequently stain the PS to determine whether the polymer nanostructure contained segmented sections.

7 Methods

Polystyrene (PS), polymethylmethacrylate (PMMA), and polyvinyl chloride (PVC) were dissolved in various solvents. PS and PMMA were dissolved in Toluene and PVC was dissolved in tetrahydrofuran (THF). Glass slides were spin coated with the polymer solutions. Porous anodized alumina oxide (AAO) was used as the template to create the nanorods. Hot plates were used to control the temperature.

Polymer solutions of various concentrations (weight percentage); such as 5%, 10%, 15% and 20%, were employed to control the thickness of the film on the glass slides. PS and PMMA were dissolved in Toluene and PVC was dissolved in THF. All solutions were mixed using a stir bar until completely dissolved. Combinations of different speeds and concentrations were explored to determine reliable control over thickness of polymer coatings on the slides. 100 mL of solution was placed on each glass slide using a pipette for spin coating. The 10% PS solution was spun at 4000 RPM for 60 seconds while the 10% PMMA solution was spun at 3000 RPM for 60 seconds. PS and PMMA alternating layers were coated on glass slides until an approximate total thickness of 1µm has been reached. AAO templates were then placed on top of the polymer thin film. The polymers were heated up to 150°C by hot plate. After polymer nanotube/nanorod fabrication, AAO templates were removed by dissolving in NaOH for an extended time. The polymer nanorod samples were cleaned and purified by centrifuge. Finally, scanning electron microscope (SEM) and transmission electron microscope (TEM) were employed to analyze the samples. The procedure for the processing of each polymer is outlined below. All samples and solutions were labeled uniquely using the format MQP2-X-Y, where X represents the page number the item was recorded on and Y is the item number on that respective page.

7.1 Materials

Polystyrene (PS) molecular weight 280,000, Sigma 01604LA
Polymethylmethacrylate (PMMA) molecular weight 996,000, Sigma 07227DH
PMMA molecular weight 120,000, Sigma 09529EH
Polyvinyl chloride (PVC) molecular weight 97,000, Sigma 11403JR
PVC molecular weight 2333,000, Sigma 01625LS
Toluene, Sigma 14774MB
2-Butanone, Sigma 360473
Compressed Nitrogen
Isopropanol, July 5th 2007
Ethanol, July 5th 2007
NaOH 0.1M, September 3rd 2007
Distilled water
Micro Cover Slides, VWR Cat. No. 483366 205
Fisherbrand Plain Microscope Slides Cat. No. 12-549
Anodisc 25 (Template), Whatman Lot No. 1120418
Disposable Scintillation Vials (Solution vial), 20 mL and 30 mL
Sealable vials, 20 mL yellow plastic vials
Bransonic Ultrasonic Cleaner (Sonicator), 2510R-MT
Genesys-s10 (UV scanner), Cat. No. 335906
Vision Lite Scan Software (UV scanning software), Version 2.1
Thermolyne 1400 Furnace, Model No. FB1415M
Spin Coater, Laurell Technologies Co. Model No. WS-6505-6NPP/Lite
Mettler Toledo Classic Plus Scale
Hot Plate
Techik Stainless Tweezers
Gel Pac Gel Box (slide holders), Lot No. 19258y/12361
Scanning Electron Microscope
Transmission Electron Microscope

7.2 Polystyrene (PS) Spin Coating

Title: Spin coating PS Thin Films

Purpose: To spin coat thin films of PS on glass cover slides. Testing various spin speeds and polymer solution concentrations to achieve evenly layered polymer films on a flat surface.

Materials:

Material	**Lot Number**	**Date Prepared**
Polystyrene	Sigma 01604LA	-
Toluene	Sigma 14774 MB	-

Process:

1. ***Solutions***

   Prepare 30 mL of each: 5, 10, 15, and 20% PS solutions in toluene

Solution ID	**Wt% PS**	**Amount of PS**	**Actual Amount**	**Toluene**
MQP2-1-001	5	1.5 g	1.5045g	30 mL
MQP2-1-002	10	3.0 g	3.0795g	30 mL
MQP2-1-003	15	4.5 g	4.5532g	30 mL
MQP2-1-004	20	6.0 g	6.0018g	30 mL

2. ***Cover Slide Pre-cleaning***
   a. Sonicate cover slide in isopropanol for 5 minutes
   b. Dry with gentle stream of N_2
   c. Sonicate cover side in acetone for 5 minutes
   d. Dry with gentle stream of N_2
3. ***Spin Coating***
   a. Place glass cover slide onto o-ring seal in spin coater
   b. Cover the glass cover slide entirely with polymer solution (~150uL)
   c. Select program 6 on the spin coater
      i. Acceleration – 10,000
      ii. Total spin time – 60 sec
      iii. Rotation speed – Variable
   d. Open N_2 valves and turn on vacuum pump to ready the sonicator. Green Start button should be illuminated when N_2 and vacuum are ready.
   e. Press start
   f. When finished, remove glass cover slide from spin coater and dry under a gentle stream of N_2, store in individually labeled slide holders
   g. Repeat steps a – f for each polymer solution
   h. After each polymer solution has been run at 500 RPM, repeat entire procedure for 750, 1000, 2000, and 3000 RPM.

After drying, all samples should be stored in small circular sample holders and labeled appropriately. Data is recorded in the table below.

Sample ID	**Solution ID and % PS**		**Rotation Speed**
MQP 2-2-005	MQP 2-1-001	5%	500 RPM
MQP 2-2-010	MQP 2-1-002	10%	500 RPM
MQP 2-2-015	MQP 2-1-003	15%	500 RPM
MQP 2-2-020	MQP 2-1-004	20%	500 RPM
MQP 2-2-006	MQP 2-1-001	5%	750 RPM
MQP 2-2-011	MQP 2-1-002	10%	750 RPM
MQP 2-2-016	MQP 2-1-003	15%	750 RPM
MQP 2-2-021	MQP 2-1-004	20%	750 RPM
MQP 2-2-007	MQP 2-1-001	5%	1,000 RPM
MQP 2-2-012	MQP 2-1-002	10%	1,000 RPM
MQP 2-2-017	MQP 2-1-003	15%	1,000 RPM
MQP 2-2-022	MQP 2-1-004	20%	1,000 RPM
MQP 2-2-008	MQP 2-1-001	5%	2,000 RPM
MQP 2-2-013	MQP 2-1-002	10%	2,000 RPM
MQP 2-2-018	MQP 2-1-003	15%	2,000 RPM
MQP 2-2-023	MQP 2-1-004	20%	2,000 RPM
MQP 2-2-009	MQP 2-1-001	5%	3,000 RPM
MQP 2-2-014	MQP 2-1-002	10%	3,000 RPM
MQP 2-2-019	MQP 2-1-003	15%	3,000 RPM
MQP 2-2-024	MQP 2-1-004	20%	3,000 RPM

7.3 Poly (methyl methacrylate) (PMMA) Spin Coating

Title: Spin coating PMMA Thin Films

Purpose: To spin coat thin films of PMMA on glass cover slides. Testing various spin speeds and polymer solution concentrations to achieve evenly layered polymer films on a flat surface.

Materials:

Material	Lot Number	Date Prepared
PMMA MW1 = 996,000	Sigma 07227DH	-
PMMA MW2= 120,000	Sigma 09529EH	-
Toluene	VWR # 48366	-

Process:

1. ***Solutions***

Prepare 30 mL of each: 5, 10, 15, and 20% PMMA MW1 solutions in toluene

Solution ID	Wt% PS	Amount of PMMA	Actual Amount	Toluene
MQP2-5-001	5	1.5 g	1.5065g	30 mL
MQP2-5-002	10	3.0 g	3.0318g	30 mL
MQP2-5-003	15	4.5 g	4.5180g	30 mL
MQP2-5-004	20	6.0 g	5.9986g	30 mL

Prepare 30 mL of each: 5, 10, 15, and 20% PMMA MW2 solutions in toluene

Solution ID	Wt% PS	Amount of PMMA	Actual Amount	Toluene
MQP2-5-005	5	1.5 g	1.5166g	30 mL
MQP2-5-006	10	3.0 g	2.9951g	30 mL
MQP2-5-007	15	4.5 g	4.5159g	30 mL
MQP2-5-008	20	6.0 g	6.0273g	30 mL

2. ***Cover slide Pre-cleaning***
   a. Sonicate cover slide in isopropanol for 5 minutes
   b. Dry with gentle stream of N_2
   c. Sonicate cover side in acetone for 5 minutes
   d. Dry with gentle stream of N_2
3. ***Spin Coating***
   a. Place glass cover slide onto o-ring seal in spin coater
   b. Cover the glass cover slide entirely with polymer solution (~150uL)
   c. Select program 6 on the spin coater
      i. Acceleration – 10,000
      ii. Total spin time – 60 sec
      iii. Rotation speed – Variable
   d. Open N_2 valves and turn on vacuum pump to ready the sonicator. Green Start button should be illuminated when N_2 and vacuum are ready.
   e. Press start

f. When finished, remove glass cover slide from spin coater and dry under a gentle stream of N_2, store in individually labeled slide holders
g. Repeat steps a – f for each polymer solution
h. After each polymer solution has been run at 500 RPM, repeat entire procedure for 750, 1000, 2000, and 3000 RPM.

After drying, all samples should be stored in small circular sample holders and labeled appropriately. Data is recorded in the table below.

Sample ID	**Solution ID and % PMMA MW1**		**Rotation Speed**
MQP2-6-001	MQP2-5-001	5%	500 RPM
MQP2-6-006	MQP2-5-002	10%	500 RPM
MQP2-6-011	MQP2-5-003	15%	500 RPM
MQP2-6-016	MQP2-5-004	20%	500 RPM
MQP2-6-002	MQP2-5-001	5%	750 RPM
MQP2-6-007	MQP2-5-002	10%	750 RPM
MQP2-6-012	MQP2-5-003	15%	750 RPM
MQP2-6-017	MQP2-5-004	20%	750 RPM
MQP2-6-003	MQP2-5-001	5%	1,000 RPM
MQP2-6-008	MQP2-5-002	10%	1,000 RPM
MQP2-6-013	MQP2-5-003	15%	1,000 RPM
MQP2-6-018	MQP2-5-004	20%	1,000 RPM
MQP2-6-004	MQP2-5-001	5%	2,000 RPM
MQP2-6-009	MQP2-5-002	10%	2,000 RPM
MQP2-6-014	MQP2-5-003	15%	2,000 RPM
MQP2-6-019	MQP2-5-004	20%	2,000 RPM
MQP2-6-005	MQP2-5-001	5%	3,000 RPM
MQP2-6-010	MQP2-5-002	10%	3,000 RPM
MQP2-6-015	MQP2-5-003	15%	3,000 RPM
MQP2-6-020	MQP2-5-004	20%	3,000 RPM

Sample ID	Solution ID and % PMMA MW2	Rotation Speed
MQP2-6-021	MQP2-5-005 5%	500 RPM
MQP2-6-026	MQP2-5-006 10%	500 RPM
MQP2-6-031	MQP2-5-007 15%	500 RPM
MQP2-6-036	MQP2-5-008 20%	500 RPM
MQP2-6-022	MQP2-5-005 5%	750 RPM
MQP2-6-027	MQP2-5-006 10%	750 RPM
MQP2-6-032	MQP2-5-007 15%	750 RPM
MQP2-6-037	MQP2-5-008 20%	750 RPM
MQP2-6-023	MQP2-5-005 5%	1,000 RPM
MQP2-6-028	MQP2-5-006 10%	1,000 RPM
MQP2-6-033	MQP2-5-007 15%	1,000 RPM
MQP2-6-038	MQP2-5-008 20%	1,000 RPM
MQP2-6-024	MQP2-5-005 5%	2,000 RPM
MQP2-6-029	MQP2-5-006 10%	2,000 RPM
MQP2-6-034	MQP2-5-007 15%	2,000 RPM
MQP2-6-039	MQP2-5-008 20%	2,000 RPM
MQP2-6-025	MQP2-5-005 5%	3,000 RPM
MQP2-6-030	MQP2-5-006 10%	3,000 RPM
MQP2-6-035	MQP2-5-007 15%	3,000 RPM
MQP2-6-040	MQP2-5-008 20%	3,000 RPM

7.4 Polyvinyl chloride (PVC) Spin Coating

Title: Spin coating PVC Thin Films

Purpose: To spin coat thin films of PVC on glass cover slides. Testing various spin speeds and polymer solution concentrations to achieve evenly layered polymer films on a flat surface.

Materials:

Material	Lot Number	Date Prepared
PVC MW1 = 97,000	Sigma 11403 JR	-
PVC MW2= 233,000	Sigma 01625 LS	-

Process:

1. ***Solutions***

   Prepare 30 mL of each: 5, 10, 15, and 20% PVC MW1 solutions in 2-Butanone

Solution ID	Wt% PS	Amount of PVC	Actual Amount	Toluene
MQP2-3-001	5	1.5 g	1.5092g	30 mL
MQP2-3-002	10	3.0 g	3.0080g	30 mL
MQP2-3-003	15	4.5 g	4.5041g	30 mL
MQP2-3-004	20	6.0 g	6.0215g	30 mL

   Prepare 30 mL of each: 5, 10, 15, and 20% PVC MW2 solutions in 2-Butanone

Solution ID	Wt% PS	Amount of PVC	Actual Amount	Toluene
MQP2-3-005	5	1.5 g	1.5155g	30 mL
MQP2-3-006	10	3.0 g	3.0115g	30 mL
MQP2-3-007	15	4.5 g	4.5340g	30 mL
MQP2-3-008	20	6.0 g	6.0238g	30 mL

2. ***Cover slide Pre-cleaning***
   a. Sonicate cover slide in isopropanol for 5 minutes
   b. Dry with gentle stream of N_2
   c. Sonicate cover side in acetone for 5 minutes
   d. Dry with gentle stream of N_2
3. ***Spin Coating***
   a. Place glass cover slide onto o-ring seal in spin coater
   b. Cover the glass cover slide entirely with polymer solution (~150uL)
   c. Select program 6 on the spin coater
      i. Acceleration – 10,000
      ii. Total spin time – 60 sec
      iii. Rotation speed – Variable
   d. Open N_2 valves and turn on vacuum pump to ready the sonicator. Green Start button should be illuminated when N_2 and vacuum are ready.
   e. Press start

f. When finished, remove glass cover slide from spin coater and dry under a gentle stream of N_2, store in individually labeled slide holders

g. Repeat steps a – f for each polymer solution

h. After each polymer solution has been run at 500 RPM, repeat entire procedure for 750, 1000, 2000, and 3000 RPM.

After drying, all samples should be stored in small circular sample holders and labeled appropriately. Data is recorded in the table below.

Sample ID	**Solution ID and % PVC MW1**	**Rotation Speed**
MQP2-4-001	MQP2-3-001 5%	500 RPM
MQP2-4-006	MQP2-3-002 10%	500 RPM
MQP2-4-011	MQP2-3-003 15%	500 RPM
MQP2-4-016	MQP2-3-004 20%	500 RPM
MQP2-4-002	MQP2-3-001 5%	750 RPM
MQP2-4-007	MQP2-3-002 10%	750 RPM
MQP2-4-012	MQP2-3-003 15%	750 RPM
MQP2-4-017	MQP2-3-004 20%	750 RPM
MQP2-4-003	MQP2-3-001 5%	1,000 RPM
MQP2-4-008	MQP2-3-002 10%	1,000 RPM
MQP2-4-013	MQP2-3-003 15%	1,000 RPM
MQP2-4-018	MQP2-3-004 20%	1,000 RPM
MQP2-4-004	MQP2-3-001 5%	2,000 RPM
MQP2-4-009	MQP2-3-002 10%	2,000 RPM
MQP2-4-014	MQP2-3-003 15%	2,000 RPM
MQP2-4-019	MQP2-3-004 20%	2,000 RPM
MQP2-4-005	MQP2-3-001 5%	3,000 RPM
MQP2-4-010	MQP2-3-002 10%	3,000 RPM
MQP2-4-015	MQP2-3-003 15%	3,000 RPM
MQP2-4-020	MQP2-3-004 20%	3,000 RPM

Sample ID	Solution ID and % PVC MW2	Rotation Speed
MQP2-4-021	MQP2-3-005 5%	500 RPM
MQP2-4-026	MQP2-3-006 10%	500 RPM
MQP2-4-031	MQP2-3-007 15%	500 RPM
MQP2-4-036	MQP2-3-008 20%	500 RPM
MQP2-4-022	MQP2-3-005 5%	750 RPM
MQP2-4-027	MQP2-3-006 10%	750 RPM
MQP2-4-032	MQP2-3-007 15%	750 RPM
MQP2-4-037	MQP2-3-008 20%	750 RPM
MQP2-4-023	MQP2-3-005 5%	1,000 RPM
MQP2-4-028	MQP2-3-006 10%	1,000 RPM
MQP2-4-033	MQP2-3-007 15%	1,000 RPM
MQP2-4-038	MQP2-3-008 20%	1,000 RPM
MQP2-4-024	MQP2-3-005 5%	2,000 RPM
MQP2-4-029	MQP2-3-006 10%	2,000 RPM
MQP2-4-034	MQP2-3-007 15%	2,000 RPM
MQP2-4-039	MQP2-3-008 20%	2,000 RPM
MQP2-4-025	MQP2-3-005 5%	3,000 RPM
MQP2-4-030	MQP2-3-006 10%	3,000 RPM
MQP2-4-035	MQP2-3-007 15%	3,000 RPM
MQP2-4-040	MQP2-3-008 20%	3,000 RPM

7.5 Multilayered Polymer Spin Coating

Title: Spin coating PMMA/PS Heterostructure Thin Films
Purpose: To spin coat thin alternating films of PMMA and PS on glass cover slides. Different layer thicknesses were used.

1. ***Solutions***

Solution ID	Wt%	Speed of Spin Coating (RPM)
MQP2-1-002	10 PS	4000
MQP2-5-006	10 PMMA	3000

2. ***Cover slide Pre-cleaning***
    a. Sonicate cover slide in isopropanol for 5 minutes
    b. Dry with gentle stream of N_2
    c. Sonicate cover side in acetone for 5 minutes
    d. Dry with gentle stream of N_2
3. ***Preparation of Slides***
    a. Place glass cover slide onto o-ring seal in spin coater
    b. Cover the glass cover slide entirely with polymer solution (~150uL)
    c. Select program 6 on the spin coater
        i. Acceleration – 10,000
        ii. Total spin time – 60 sec
        iii. Rotation speed – Refer to chart
    d. Open N_2 valves and turn on vacuum pump to ready the sonicator. Green Start button should be illuminated when N_2 and vacuum are ready.
    e. Press start
    f. When finished, remove glass cover slide from spin coater and dry under a gentle stream of $N_{2,}$ store in individually labeled slide holders
    g. Repeat steps a – f for each polymer solution
    h. After the initial polymer solution has been run at the desired speed, repeat entire procedure for additional polymer layers on top of the same slide.

4. Slide Layer Distribution

	Layer	**Plastic**
MQP2-8-001 **MQP2-10-001** **MQP2-10-002**	Layer 1	PS
	Layer 2	PMMA
	Layer 3	PS
	Layer 4	PMMA
	Layer 5	PS
	Layer 6	PMMA
	Layer 7	PS
	Layer 8	PMMA
	Layer 9	PS
	Layer 10	PMMA
MQP2-8-002 **MQP2-10-003** **MQP2-10-004**	Layer 1	PS
	Layer 2	PS
	Layer 3	PMMA
	Layer 4	PMMA
	Layer 5	PS
	Layer 6	PS
	Layer 7	PMMA
	Layer 8	PMMA
	Layer 9	PS
	Layer 10	PS
MQP2-8-003 **MQP2-10-005** **MQP2-10-006**	Layer 1	PS
	Layer 2	PS
	Layer 3	PS
	Layer 4	PS
	Layer 5	PS
	Layer 6	PMMA
	Layer 7	PMMA
	Layer 8	PMMA
	Layer 9	PMMA
	Layer 10	PMMA

Slide	**Layer**	**Plastic**
MQP2-10-007 **MQP2-10-008**	Layer 1	PS
	Layer 2	PS
	Layer 3	PS
	Layer 4	PS
	Layer 5	PS
	Layer 6	PS
	Layer 7	PS
	Layer 8	PS
	Layer 9	PS
	Layer 10	PS
MQP2-10-009 **MQP2-10-010**	Layer 1	PMMA
	Layer 2	PMMA
	Layer 3	PMMA
	Layer 4	PMMA
	Layer 5	PMMA
	Layer 6	PMMA
	Layer 7	PMMA
	Layer 8	PMMA
	Layer 9	PMMA
	Layer 10	PMMA

7.6 Creating nanorods

Title: Creating nanorods
Purpose: To fabricate nanorods through template wetting.
Materials:

Material	Lot Number	Date Prepared
Samples from 8.1-8.6	-	1/22/08-3/31/08
Anodisc 25 (template)	1120418	-

Process:

1. ***Preparation***
    a. Remove the ceramic center from the plastic outer ring of an individual anodisc.
        i. Prevents the outer ring from melting and filling the pours of the template.
    b. Place the template on the sample and top with a cover slide.
    c. Prepare 3 samples in this manor and line them up side by side between two Fisherbrand Plain Microscope Slides.
2. ***Heating***
    a. Preheat the hot plate to 150 C.
    b. Place your prepared samples on the center of the hot plate, with approximately ½ a kilogram of weight on top to create pressure, for 72 hours.
3. ***Removal of rods from the template***
    a. Remove the heated slides from the hot plate and place in water to loosen the glass from the plastic.
    b. Put the plastic layer and template in a small 2 mL sealable vial filled with NaOH and sonicate it for approximately 30 minutes to break up the template and knock the rods off of the sheet of plastic.
    c. Centrifuge the already sonicated sample for 10 to 15 minutes.
    d. Remove the large pieces of plastic from the vial and pipette out the NaOH.
    e. Fill the vial with distilled water and centrifuge for only 5 minutes.
    f. Pipette off the water, fill with ethanol and shake thoroughly.
4. ***Dying Samples to distinguish between PMMA and PS within a single rod.*** (Huibers, 1977)
    a. Combine $RuCl_33H_2O$ with NaOCl to form RuO_4. Use caution due to the toxicity of the gas emitted.
    b. The gas will stain PS to be a darker color, allowing visual discrimination.
    c. The sample solutions are then ready to be viewed through a TEM or SEM.

7.7 Determining the Thickness of PMMA Layers

Title: Finding empirical thicknesses for PMMA spin coating

Purpose: To determine the thickness of PMMA layers, created during spin coating, based on solution concentrations and rotation velocity.

Materials:

Material	Lot Number	Date Prepared
2-Butanone		-
PMMA MW: 120,000	Sigma 09529EH	-

Process:

1. ***Solutions***

   Prepare 20 mL of 10 and 20% PS and PMMA solutions in Toluene.

Solution ID	Wt% Plastic	Amount of Plastic (g)	Actual Amount (g)	20 mL of Solvent
MQP2-15-001	10 PMMA	2	1.9917	Butanone
MQP2-15-002	5 PMMA	1	1.0035	Butanone
MQP2-15-003	15 PS	3	3.0014	Butanone

2. ***Cover slide Pre-cleaning***
   a. Sonicate cover slide in isopropanol for 5 minutes
   b. Dry with gentle stream of N_2
   c. Sonicate cover side in acetone for 5 minutes
   d. Dry with gentle stream of N_2
3. ***Spin Coating***
   a. Place glass cover slide onto o-ring seal in spin coater
   b. Cover the glass cover slide entirely with polymer solution (~150uL)
   c. Select program 6 on the spin coater
      i. Acceleration – 10,000
      ii. Total spin time – 60 sec
      iii. Rotation speed – Variable
   d. Open N_2 valves and turn on vacuum pump to ready the sonicator. Green Start button should be illuminated when N_2 and vacuum are ready.
   e. Press start
   f. When finished, remove glass cover slide from spin coater and dry under a gentle stream of $N_{2,}$ store in individually labeled slide holders
   g. Repeat steps a – f for each polymer solution
   h. After the initial polymer solution has been run at the desired speed, repeat entire procedure for additional samples at the desired rotation speed with the samples listed below.

Sample	Rotation Speed
MQP2-18-001	500
MQP2-18-002	500
MQP2-18-003	500
MQP2-18-004	1000
MQP2-18-005	1000
MQP2-18-006	1000
MQP2-18-007	2000
MQP2-18-008	2000
MQP2-18-009	3000
MQP2-18-010	3000
MQP2-18-011	1000
MQP2-18-012	1000
MQP2-18-013	1000
MQP2-18-014	2000
MQP2-18-015	2000
MQP2-18-016	3000
MQP2-18-017	3000
MQP2-18-018	1000
MQP2-18-019	1000
MQP2-18-020	1000
MQP2-18-021	2000
MQP2-18-022	2000
MQP2-18-023	3000
MQP2-18-024	3000

4. ***Thickness Calculation***
    a. Run each sample through the UV scanner, using Vision Lite Scan V. 2.1, over the interval 300-1100 micro meters with values every 2 micrometers.
    b. Set the “Spectrophotometer measurement mode” to A.
    c. Restrict the Y axis to a minimum of 0 and a maximum of 0.05 with overlay.
    d. Set the “Peak Pick Threshold” to 0.01 A.
5. ***Apply your found values to an equation.***
    a. Measures the distance between two peaks, endpoints are labeled as V1 and V2.
    b. $d = \frac{m}{(2D_n\sqrt{n^2}-(\sin\theta)^2} \text{ (Huibers, 1977)}$

$$D_n = \frac{1}{v_1} - \frac{1}{v_2}$$

M = number of peaks generated on absorbance versus wavelength graph
N = refractive index (1.489 for PMMA)
θ = angle of incidence (.7854 radians)

D = thickness (units of nm)
V_n= incidence of peak (nm)

c. Create a thickness verses rotation speed concentration plot
   i. Fit each curve to the equation $y = -A * \ln x + B$
d. Plot the Concentration of PMMA against the value of the log equation parameters.

7.8 Determining the Effects of Changing Thickness and Temperature on Nanorod Development

Process:

1. ***Solutions***

Prepare 20 mL of 10 and 20% PS and PMMA solutions in Toluene.

Solution ID	Wt% Plastic	Amount of Plastic (g)	Actual Amount (g)	20 mL of Solvent
MQP2-15-001	10 PMMA	2g	19938g	2-Butanone

2. ***Cover Slide Pre-cleaning***
   a. Sonicate cover slide in isopropanol for 5 minutes
   b. Dry with gentle stream of N_2
   c. Sonicate cover side in acetone for 5 minutes
   d. Dry with gentle stream of N_2
3. ***Spin Coating***
   a. Place glass cover slide onto o-ring seal in spin coater
   b. Cover the glass cover slide entirely with polymer solution (~150uL)
   c. Select program 6 on the spin coater
      i. Acceleration – 10,000
      ii. Total spin time – 60 sec
      iii. Rotation speed – 1000 RPM
   d. Open N_2 valves and turn on vacuum pump to ready the sonicator. Green Start button should be illuminated when N_2 and vacuum are ready.
   e. Press start
   f. When finished, remove glass cover slide from spin coater and dry under a gentle stream of $N_{2,}$ store in individually labeled slide holders
   g. Repeat steps a – f for each polymer solution
   h. After the initial polymer solution has been run at the desired speed, repeat entire procedure to add additional layers to the samples listed below.

Sample ID	Solution ID	Rotation Speed (RPM)	Number of layers	Temperature (C)	Duration of Heating (hr)
MQP2-16-001	MQP2-15-001	1000	1	150	6
MQP2-16-002	MQP2-15-001	1000	2	150	6
MQP2-16-003	MQP2-15-001	1000	4	150	6
MQP2-16-004	MQP2-15-001	1000	1	150	24
MQP2-16-005	MQP2-15-001	1000	2	150	24
MQP2-16-006	MQP2-15-001	1000	4	150	24
MQP2-16-007	MQP2-15-001	1000	1	150	48
MQP2-16-008	MQP2-15-001	1000	2	150	48
MQP2-16-009	MQP2-15-001	1000	4	150	48
MQP2-16-010	MQP2-15-001	1000	1	200	6
MQP2-16-011	MQP2-15-001	1000	2	200	6
MQP2-16-012	MQP2-15-001	1000	4	200	6
MQP2-16-013	MQP2-15-001	1000	1	200	24
MQP2-16-014	MQP2-15-001	1000	2	200	24
MQP2-16-015	MQP2-15-001	1000	4	200	24
MQP2-16-016	MQP2-15-001	1000	1	200	48
MQP2-16-017	MQP2-15-001	1000	2	200	48
MQP2-16-018	MQP2-15-001	1000	4	200	48

4. ***Sample preparation***
   a. Remove the ceramic center from the plastic outer ring of an individual anodisc.
      i. Prevents the outer ring from melting and filling the pours of the template.
   b. Place the template on the sample and top with a cover slide.
   c. Prepare 3 samples in this manor and line them up side by side between two Fisherbrand Plain Microscope Slides.
5. ***Heating***
   a. Preheat the hot Thermolyne 1400 Furnace to the temperature indicated in the chart above.
   b. Place your prepared samples on the center of the furnace, with approximately ½ a kilogram of weight on top, for the predetermined length of time.
6. ***Removal of rods from the template***
   a. Remove the heated slides from the furnace and place in water to loosen the glass from the plastic.
   b. Put the plastic layer and template in a small 2 mL sealable vial filled with NaOH and sonicate it for approximately 30 minutes to break up the template and knock the rods off of the sheet of plastic.
   c. Centrifuge the already sonicated sample for 10 to 15 minutes.
   d. Remove the large pieces of plastic from the vial and pipette out the NaOH.
   e. Fill the vial with distilled water and centrifuge for only 5 minutes.
   f. Pipette off the water, fill with ethanol and shake thoroughly.

The sample solutions are then ready to be viewed through a TEM or SEM.

8 Results

8.1 Determining Desired Rotation Speeds for Spin Coating Each Plastic

After preparing one hundred twenty slides and testing them at various speeds, it was found that at higher concentrations and lower speeds, the spin coating process resulted in a highly uneven coating. The following pictures demonstrate the typical results at low spin speeds, high solute concentration, and the minimization of these effects by accordingly varying the spin speed and concentration. At low speeds the highly uneven coating resulted in thicker layers in the center of the slide and greatly varied thicknesses towards the edge of the slide. At higher concentrations precipitate was still in the solution as it was unable to completely dissolve and resulted in speckling on the slides. A minimization of these effects can be seen in Figure 8, where a more uniform coating is seen and no precipitate is visible.

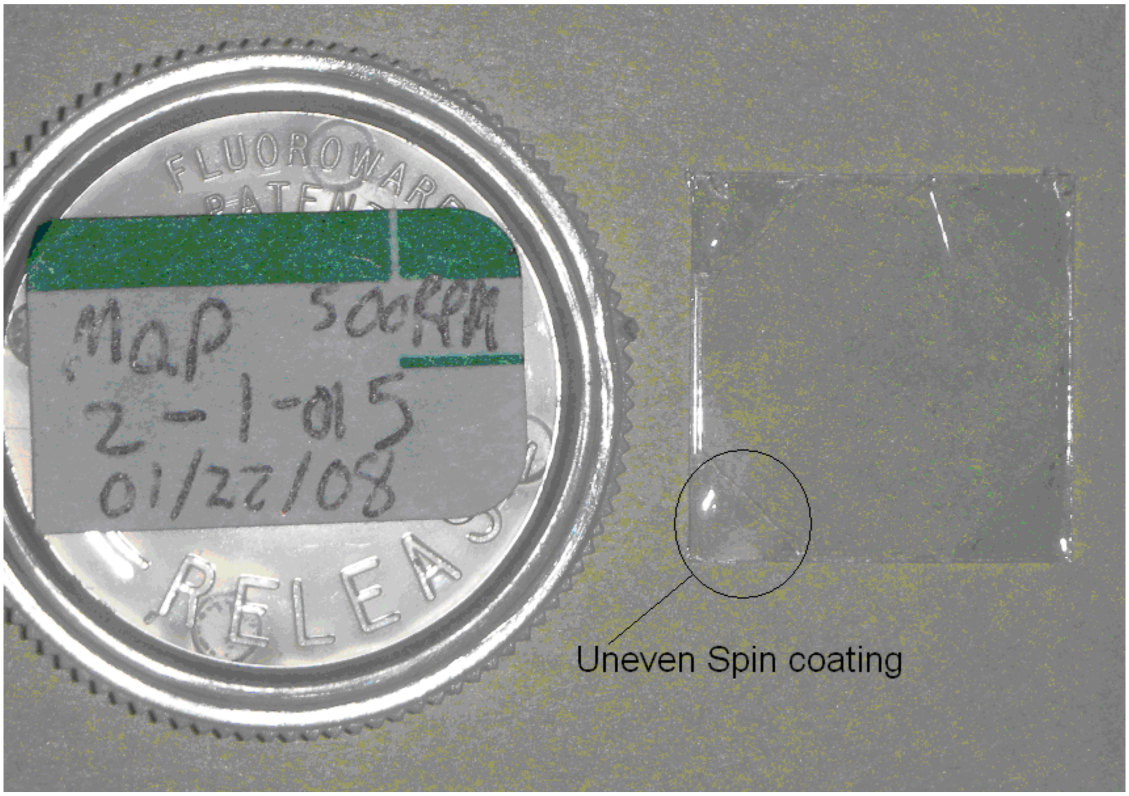

Figure 8 - 15% PS in toluene spin coated at 500 RPMs demonstrates an unevenly distributed layer caused by low speeds (incorectly labed, should be MQP2-2-015).

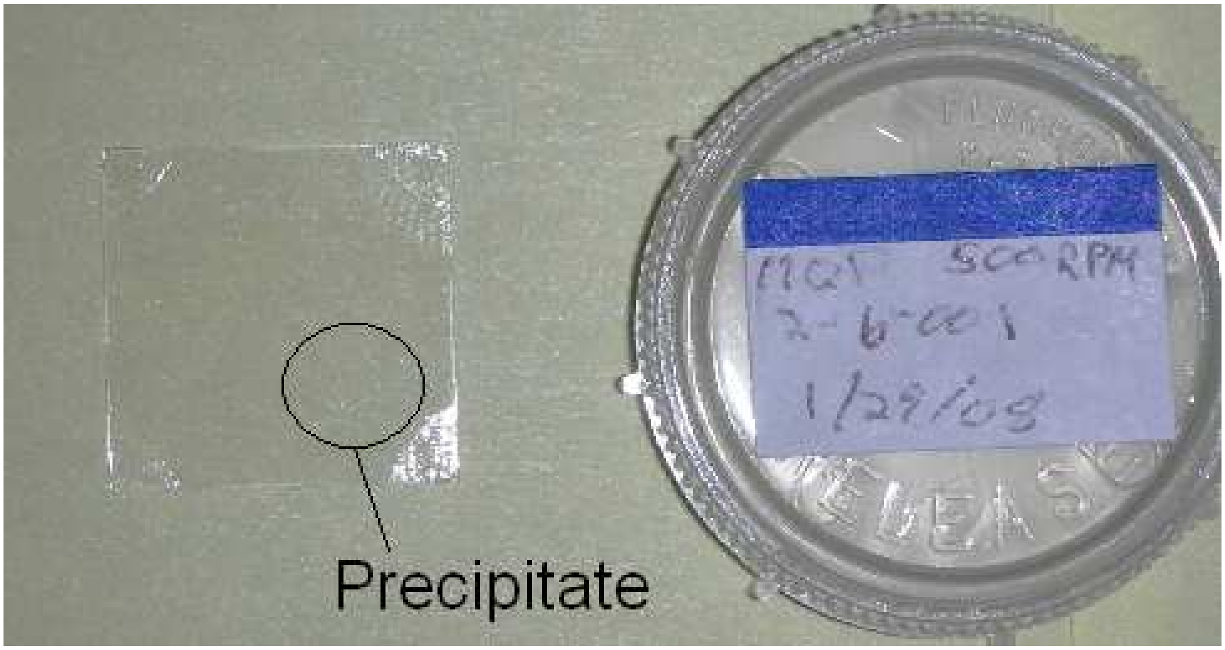

Figure 9 - 5% PMMA in toluene spin coated at 500 RPMs shows the same uneven coating demonstrated in figure 6 along with precipitated due to exceeding saturation for toluene.

Figure 10 - 15% PS in toluene spin coated at 2000 RPMs exemplifies a desired rotation speed for the given concentration of plastic. The spin coating appears visually even and there is no precipitate on the slide (incorrectly labeled, should be MQP2-2-018).

8.2 Determining the thickness of PMMA layers

After creating two to three slides for each rotation speed and concentration, the thicknesses of each slide were calculated using UV-vis spectroscopy (Huibers, 1977). The results are seen below with the averages of numerous samples used as the accepted value. At higher concentrations it was seen that the average thickness of the slide was greater. At higher speeds the thickness of the slides was lower compared to lower speed slides. The graph below depicts polymer thickness curves as a function of spin speed and concentration.

Table 2-Solutions used to create PMMA thin film layers.

Mass(g) PMMA	Real Mass (g) PMMA	MEK (mL)	(%) weight/volume
1.0g	1.0191g	20 mL	5%
2.0g	2.0162g	20 mL	10%
3.0g	3.0006g	20 mL	15%

Table 3-PMMA thin film layer thicknesses verses solution concentration and rotation speed.

Concentration	Rotation Speed	Peaks	V1	V2	Dn	d(nm)	average (nm)	StDEV (nm)
5% PMMA	500	1	302	326	0.000244	1565.248	1434.7633	193.230738
	500	1	800	1000	0.00025	1526.264		
	500	2	610	990	0.000629	1212.778		
	1000	3	306	930	0.002193	522.0485	511.550808	17.7093451
	1000	3	306	932	0.002195	521.4997		
	1000	3	302	1020	0.002331	491.1043		
	2000	3	306	998	0.002266	505.1693	499.180118	8.46992437
	2000	3	306	1056	0.002321	493.191		
	3000	2	302	852	0.002138	357.0127	349.428931	10.7250284
	3000	2	304	946	0.002232	341.8452		
10% PMMA	1000	1	770	1098	0.000388	983.5332	979.818683	104.90613
	1000	1	692	992	0.000437	873.1046		
	1000	2	610	1070	0.000705	1082.818		
	2000	3	306	920	0.002181	524.846	600.687524	107.256057
	2000	1	302	364	0.000564	676.529		
	3000	3	304	1064	0.00235	487.1836	485.523116	2.3482792
	3000	3	303	1070	0.002366	483.8626		
15% PMMA	1000	1	658	858	0.000354	1077.092	1075.77916	30.120105
	1000	2	618	1078	0.00069	1105.221		
	1000	2	610	1100	0.00073	1045.024		
	2000	1	630	1006	0.000593	643.1621	712.096828	97.4883696
	2000	1	694	1050	0.000489	781.0315		
	3000	1	618	1006	0.000624	611.3987	606.603758	6.78108366
	3000	2	410	854	0.001268	601.8088		

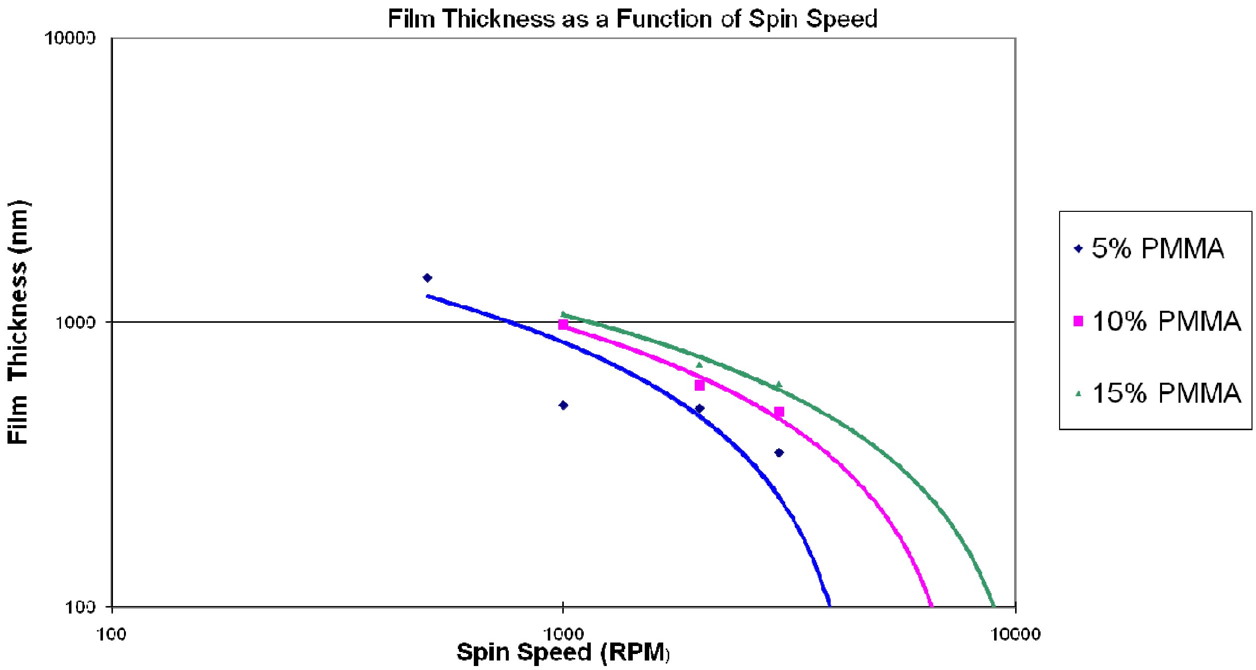

Figure 11 - Polymer thin film thickness curves as determined by UV-vis spectroscopy and application of a known equation.

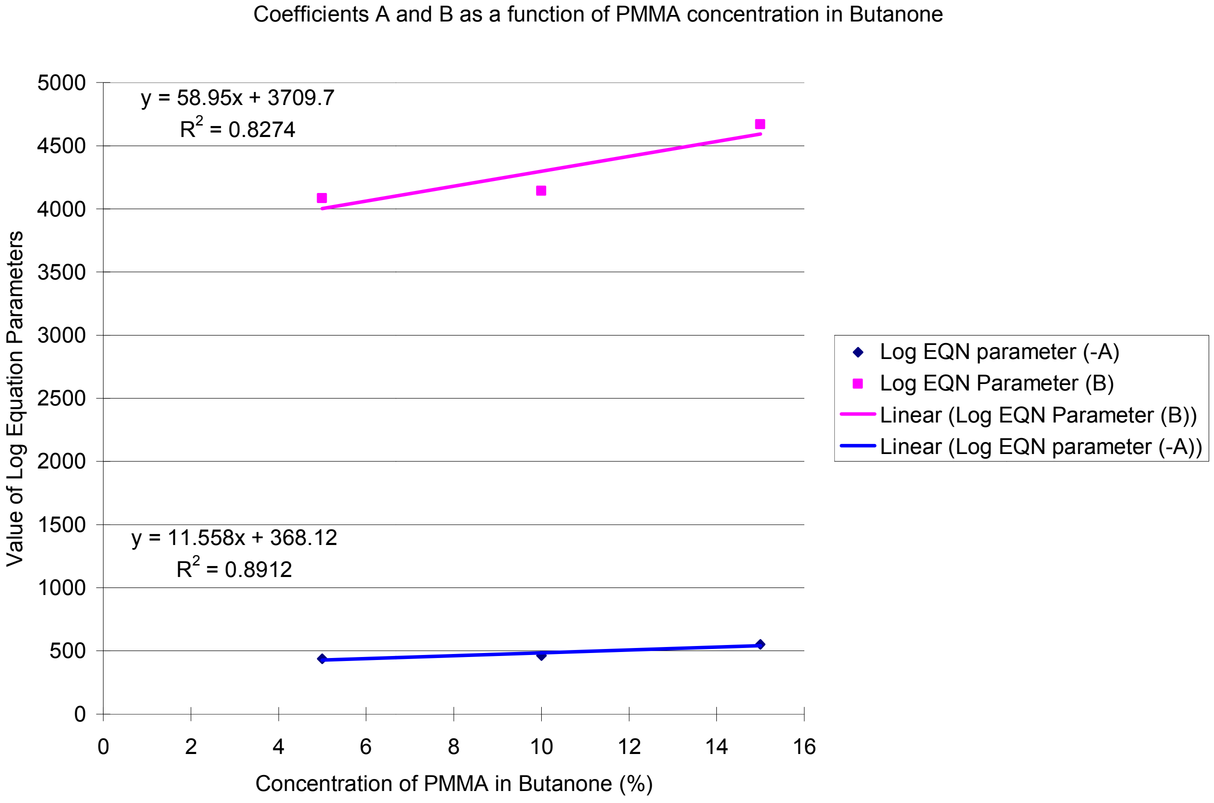

Figure 12 -Experimental Data fit Logarithmic Trend: B. This graph shows the coefficients A and B as a function of PMMA concentration in 2-Butanone.

8.3 Creating nanorods

The creation of nanorods was performed by template wetting. As seen in the TEM pictures below, the successful fabrication of heterostructure polymer nanorods was performed. In Figure 15, the alternating segments of PS and PMMA can be seen due to the staining of PS by gas emitted by RuO_4 which provides a contrast against the PMMA which is not stained. The structure and size of the nanorods is visible as well in Figure 11 and Figure 12.

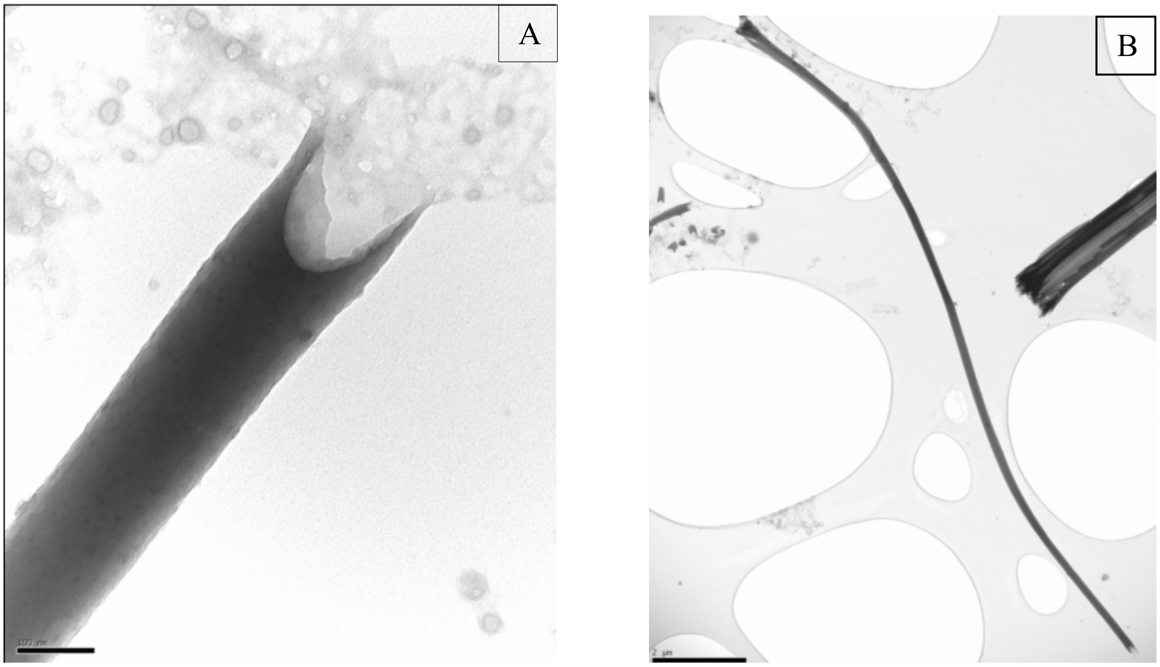

Figure 13 – (A)TEM picture of the side of a PS nanorod illustrates the dimple effect at the tip. Shown against a scale of 100 nanometers. (B) A single nanorod of PS shown against a scale of 2 micrometers to demonstrate the length of a single rod created through AAO template wetting.

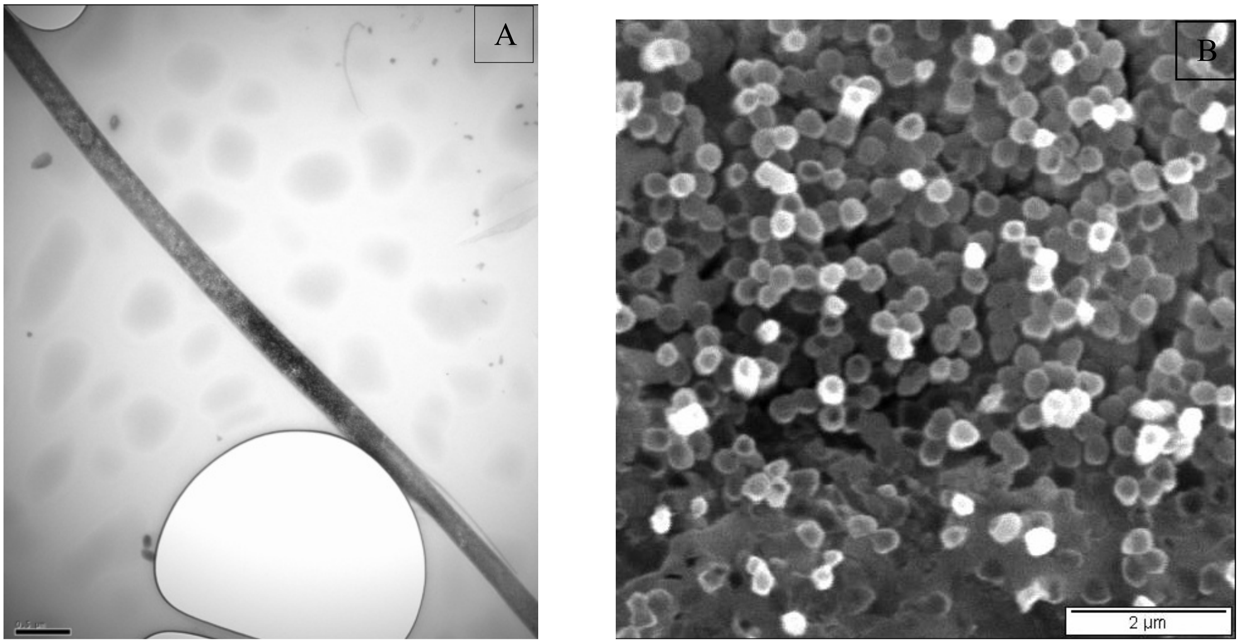

Figure 144 – (A) TEM picture of a PS and PMMA layered nanorod. (B) A top down SEM image of several nanorods resting against each other after the template was removed.

8.4 Determining the effects of changing temperature and thickness on nanorod development.

The template wetting of polymer nanorods at various time and temperatures was performed. The results, as seen below, indicate that at longer timescales the length of the rods are unaffected as the pores are completely filled. Furthermore, it appeared that at higher polymer thickness, the walls of the tubes created were thinner. There was not conclusive evidence, however, to support this claim as the wall thicknesses of the rods varied greatly. It is thought that the thickness difference may be correlated to the electron beam of the TEM that affects the polymer at greater magnifications. Also, there was particulate seen inside the tubes that was unidentified and is of further interest as it may have resulted from the wetting process or the handling of the polymer samples in preparation for imaging. Further testing to clarify the effects of time and temperature will allow greater understanding of the process.

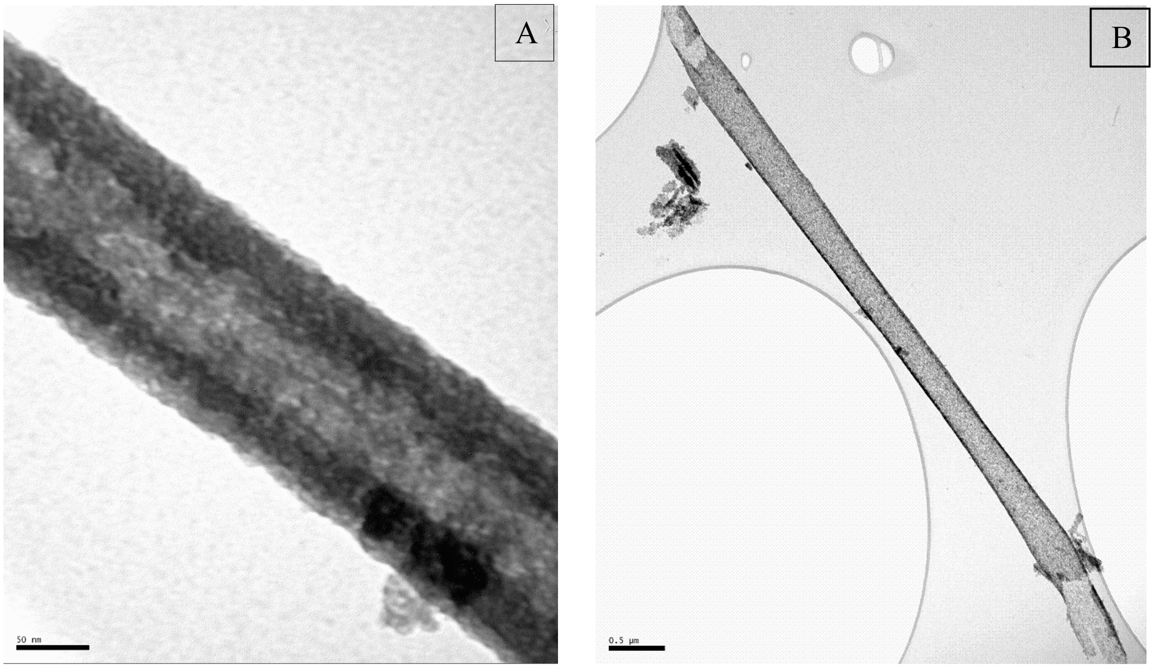

Figure 15 –(A) 1-layer PMMA heated at 150C for 48 hours. (B) 2-layer PMMA heated at 150C for 48 hours.

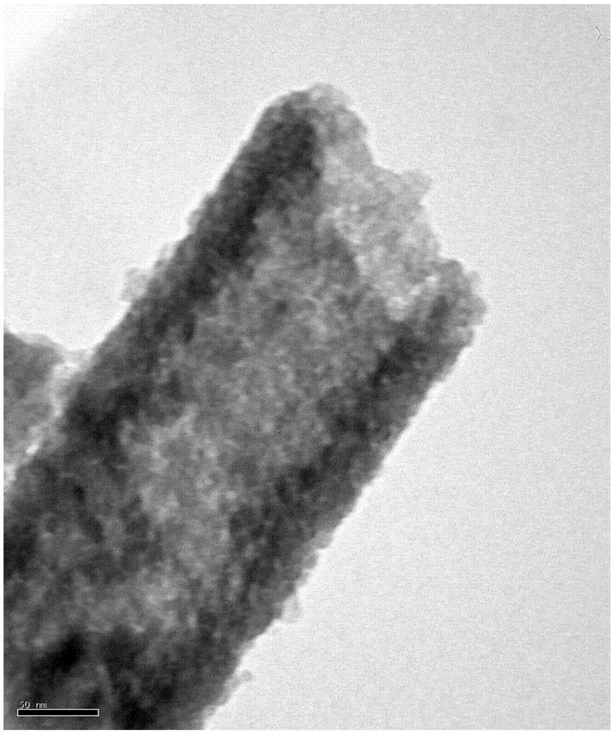

Figure 16 - 4-layer PMMA heated at 150C for 48 hours.

9 Analysis

9.1 Spin coating of slides

Sections 7.2 to 7.4 of this report discuss how each solution and slide was spin coated. Varying solutions were tested at multiple rotation speeds. The goal of doing this was to determine a solution percentage, by weight, and rotation speed that would produce an evenly coated slide. Even slide coating helps to limit the variables when multiple layers of polymer are all placed on a single slide.

Low rotation speeds produced uneven coating on the edges of the slide. The uneven coating prevents the ability to predict the thickness of the plastic layers at the contact point between the AAO template and the polymer. Uneven spin coating due to low rotation speeds is exhibited in figure 6. Rotation speeds below 1000 RPMs for all polymers used in this experiment resulted in uneven coating, thus, no speed below 1000 RPMs for any polymer was used for the remainder of the experiment.

Each solution used in sections 7.2 to 7.4 were prepared and stirred over night before they were used to spin coat each sample. All solutions from 5-20%, by weight, of PS were fully dissolved and showed no precipitate on the slides after spin coating. PMMA, as seen in Figure 7, left small particles on the slide which was caused by trace precipitate, in the solution, that was not visible until after spin coating. To eliminate the precipitate, PMMA was dissolved in 2-butanone for any further samples. PVC solutions had a similar problem to that of PMMA solutions in toluene, except that the majority of the PVC would precipitate out leaving a solid block within the solution bottles. PVC was dissolved in toluene, 2-butanone and tetrahydrofuran with the same results. Since no solvent readily available within the lab could produce a fully dissolved solution, above 0.5% by weight, no PVC slides were used to create nanorods. All the

PVC solutions and samples were properly disposed of and were not used for the remainder of the experiment.

Sample MQP2-2-18, Figure 8, exemplifies what a slide should look like. There is a visible layer of polymer on the glass slide, only noticeable due to the fine strings of plastic extending off the corners of the slide. The layer is consistent across the entirety of the slide and has no visible precipitate.

9.2 Determination of thin film thickness

In order to determine the thickness of the thin film layers on the slide they were measured using UV-vis technology. This was done to limit the variables in the experiment and to use predetermined polymer thicknesses on the slide. Data points were recorded and condensed down into a graph. The graph used to predict the thickness of each layer was created based on a known method which was previously used in literature to measure the thickness of layers of another material (Huibers, 1977). In order to determine the thicknesses created at varying speeds, single layer samples of PMMA were created at varying weight percentages. Multiple samples were created and an average value was taken as the agreed upon thickness at a given speed.

The wetting of the polymer occurs at temperatures above the glass transition temperature. By varying the time and temperature we attempted to control the amount of wetting in the porous template. This would allow the controlled production of known length nanorods.

Three films were created at each weight percentage for each speed chosen. The result can be seen in Table 4. The following formulae were used in calculating the thickness of each layer.

$$d = \frac{m}{(2D_n\sqrt{n^2} - (\sin\theta)^2} \text{ (Huibers, 1977)}$$

$$D_n = \frac{1}{v_1} - \frac{1}{v_2}$$

M = number of peaks generated on absorbance versus wavelength graph
N = refractive index (1.489 for PMMA)
θ = angle of incidence (.7854 radians)
D = thickness (units of nm)
V_n= incidence of peak (nm)

Table 4 - Thicknesses of various % weight solutions after UV-vis spectroscopy.

Concentration	Rotation Speed	Peaks	W1	W2	D_n	d(nm)	average (nm)	StDEV (nm)
5% PMMA	500	1	302	326	0.000244	1565.248	1434.7633	193.230738
	500	1	800	1000	0.00025	1526.264		
	500	2	610	990	0.000629	1212.778		
	1000	3	306	930	0.002193	522.0485	511.550808	17.7093451
	1000	3	306	932	0.002195	521.4997		
	1000	3	302	1020	0.002331	491.1043		
	2000	3	306	998	0.002266	505.1693	499.180118	8.46992437
	2000	3	306	1056	0.002321	493.191		
	3000	2	302	852	0.002138	357.0127	349.428931	10.7250284
	3000	2	304	946	0.002232	341.8452		
10% PMMA	1000	1	770	1098	0.000388	983.5332	979.818683	104.90613
	1000	1	692	992	0.000437	873.1046		
	1000	2	610	1070	0.000705	1082.818		
	2000	3	306	920	0.002181	524.846	600.687524	107.256057
	2000	1	302	364	0.000564	676.529		
	3000	3	304	1064	0.00235	487.1836	485.523116	2.3482792
	3000	3	303	1070	0.002366	483.8626		
15% PMMA	1000	1	658	858	0.000354	1077.092	1075.77916	30.120105
	1000	2	618	1078	0.00069	1105.221		
	1000	2	610	1100	0.00073	1045.024		
	2000	1	630	1006	0.000593	643.1621	712.096828	97.4883696
	2000	1	694	1050	0.000489	781.0315		
	3000	1	618	1006	0.000624	611.3987	606.603758	6.78108366
	3000	2	410	854	0.001268	601.8088		

The equations used to create the lines of best fit in Figure 6 had a very high correlation to the data points with an R^2 value over 0.84. The high R^2 value correlates the accuracy of the model equation to the data points. The linear correlation between the coefficients of the lines of best fit and the concentration thicknesses, demonstrated in Figure 7, proves that the equation can be applied to PMMA in determining the thickness using UV-vis.

9.3 *Fabrication and analysis of nanostructures*

Figure 9 demonstrates the length of one of our longer, single layered, PS nanorods, approximately 16 micrometers. The rod lenghts vary due to the sonicating proccess used to break them free of the template and remaining polymer layers left over after the template wetting. Before sonicating the rods rest limply against each other while attached at the base to the remaining polymer layer on the converslide as seen in Figure 11. Multilayered rods were characterized using RuO_4 stain to darken PS layers so that they could be visually discriminated against PMMA. Our first hypothesis, that multilayered thin films would create multilayered nanorods, was strongly supported by Figure 10 displaying a darkened layer of PS surrounded by two lighter regions of PMMA.

The second hypothesis of this project was that varying the thickness of each layer on a slide would cause sections of alternating polymers, in a single nanorod, to have a predictable length. These layers were created by spin coating glass slides at a set RPM value with a single weight percentage solution of polymer. Multiple coatings could be performed to create thicker films. Film thicknesses of a single layer were determined as a baseline and graphs developed to predict film thicknesses at higher RPMs. The rods created had various thicknesses, predictable given the characteristic equation determined by UV-vis spectroscopy and were subsequently heated for 6, 24 and 48 hours at both 150 and 200 degrees Celsius. The lengths of the rods however, were found to be consistent over all time periods due to the long wetting time. Further wetting at lower times and temperatures may create greater variability and allow differentiation between lengths at different times and temperatures. The thickness of the tube walls was found to be thinner at higher thicknesses, which was opposite the thinking that a greater amount of material would fill the pores more completely. Also, as seen in the Appendices, there was a large amount of unknown material that filled the tubes and the source was undetermined.

10 Conclusions

The development of nanotechnology has introduced both risk and reward in the form of stronger, more applicable materials, but the unknown long-term effects of their use. The increased control over nanosized materials has allowed a new field of materials with unique characteristics in relation to their bulk counterparts.

Polymer nanorods were created with homostructures and heterostructures. Homostructure rods have consistent properties for the entirety of the rod where multilayered nanorods can have their properties adjusted based on the different polymers inserted into the rod and the order in which they are placed.

Due to the long time scales tested, the effect of time on nanostructures was unable to be determined and the similar size and structure has been obtained on all samples. The rod lengths were all similar due to the complete filling of the AAO template. A relationship between polymer thin film thickness and nanostructure composition was not determined as varied results were received at all thicknesses. While several samples appeared to have thinner walls it was not concluded whether it was resulted from the polymer film thickness or other variable. By performing the tests again over shorter timescales, it may be possible to elucidate a more precise relationship between time, temperature, and film thickness.

In principle, we expect the template assisted polymer wetting technique used to be expandable to any polymer and any number of polymers at the same time, including bioresorbable polymers. Scaling the fabrication of heterostructure nanorods is very affordable and can be easily accomplished should template-assisted wetting be used.

Increasing the control of the properties exhibited by nanorods gives them great promise in the areas of scaffolding for tissue engineering and even as electrical components in sensing equipment.

11 Future Recommendations

Based on our successful fabrication of heterostructure polymer nanorods, we would like to suggest to look into the fabrication of a wider array of polymers is investigated and their properties established. The addition of numerous additional polymers into a single heterostructure nanorod allows for greater control of material properties. The investigation into the use of nanorods for biomedical applications as well as the utilization of biomedical polymers in heterostructure nanorods should be pursued. Further characterization of polymer film thicknesses and time and temperature dependency of nanorod fabrication should be performed to better control the process of template wetting.

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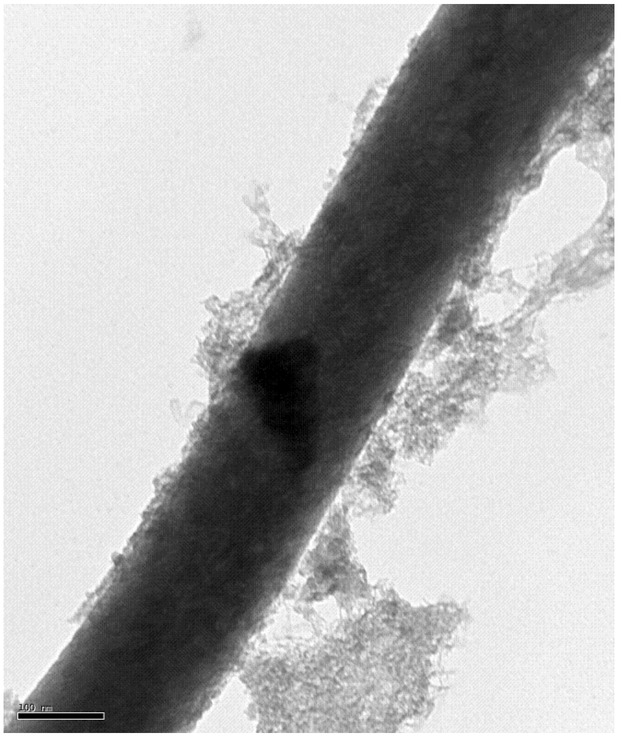
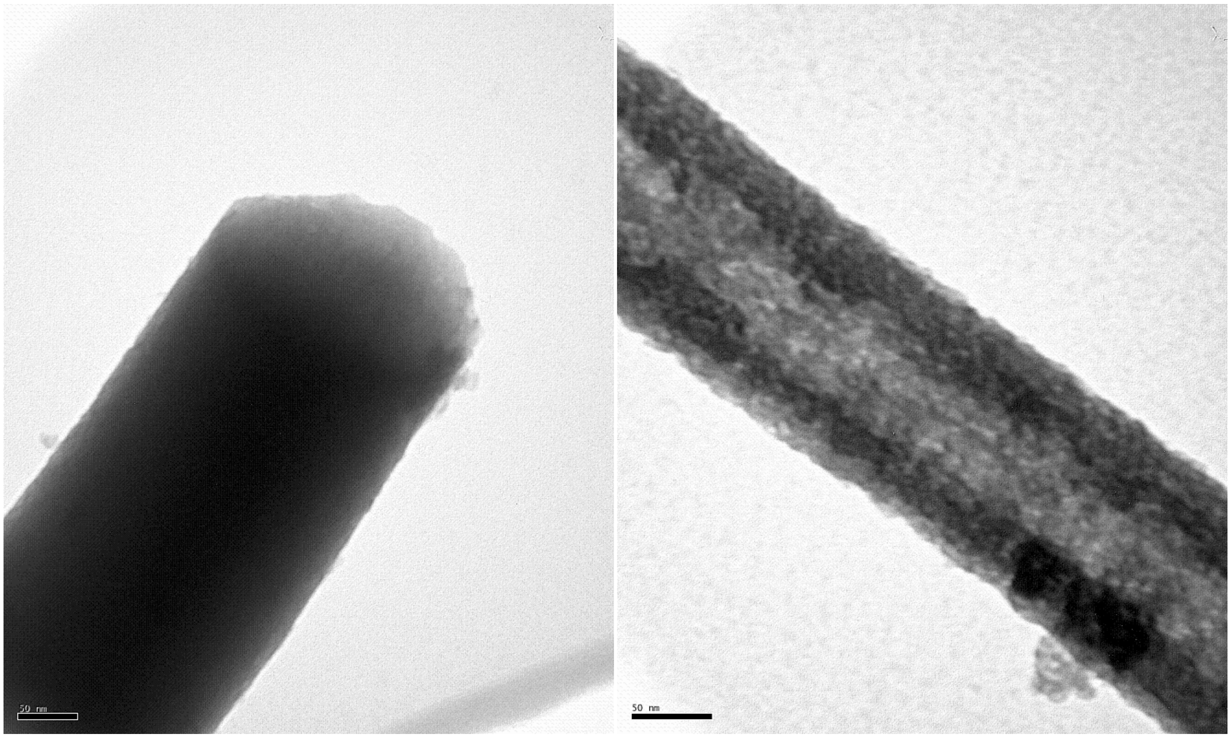
13 Appendix

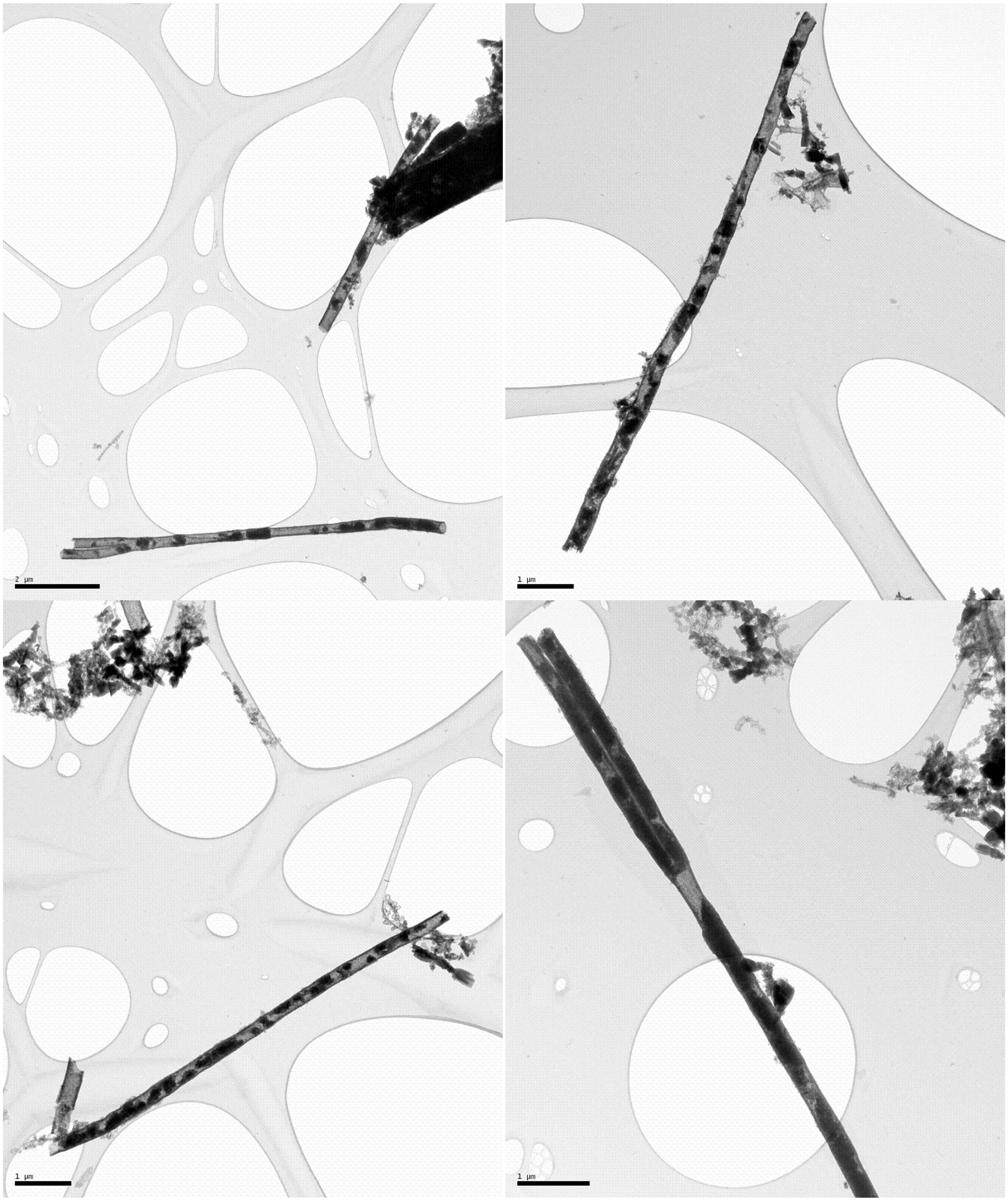
The following TEM images were all taken from samples heated at 150C and for 48 hours. They are included to illustrate results from the wetting process in addition to the typical results presented in Sections8.3 and 8.4 .

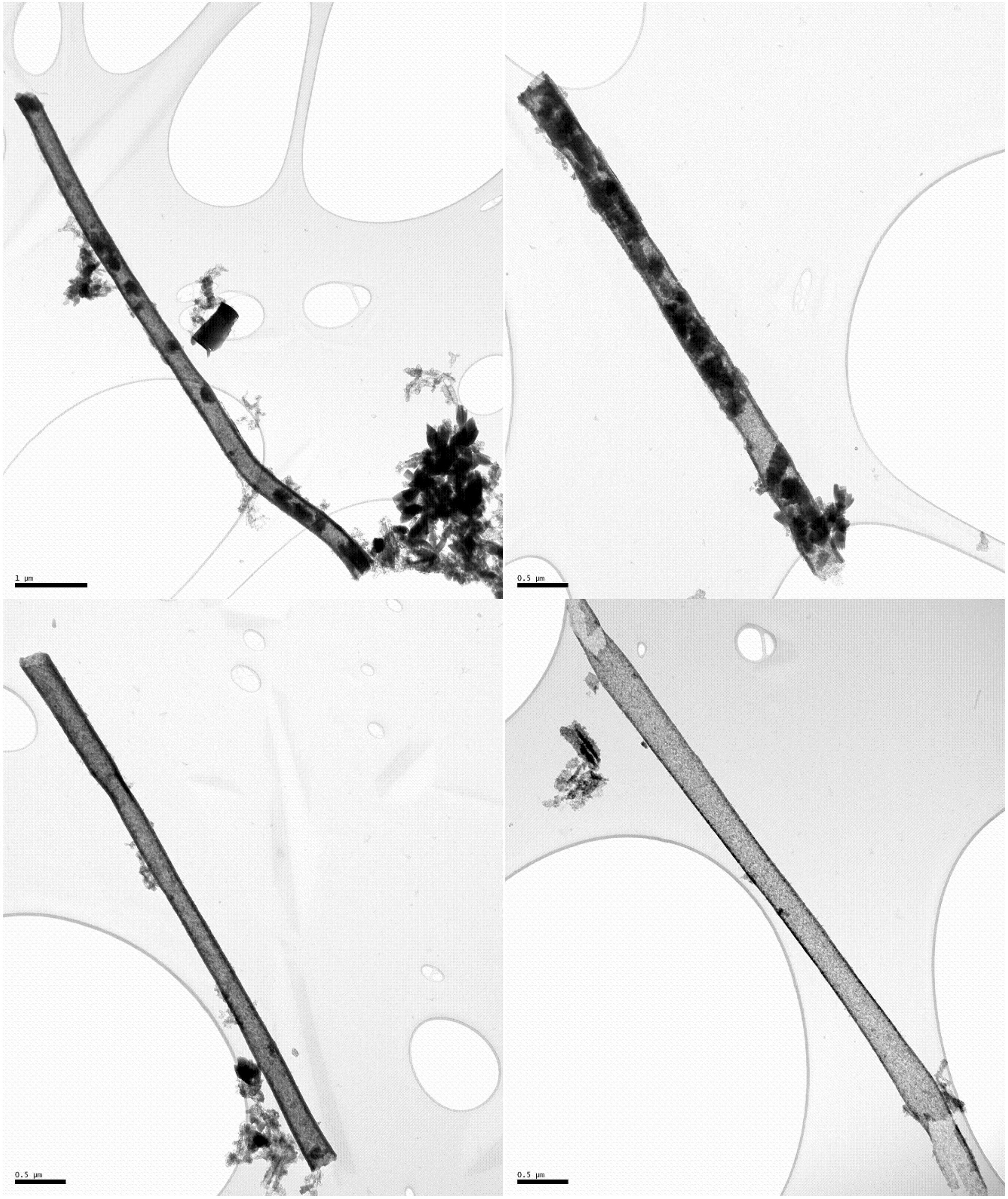
13.1 TEM Images of 1-layer PMMA at 150C




50 nm
50 nm

13.2 TEM Images of 2-layer PMMA at 150C

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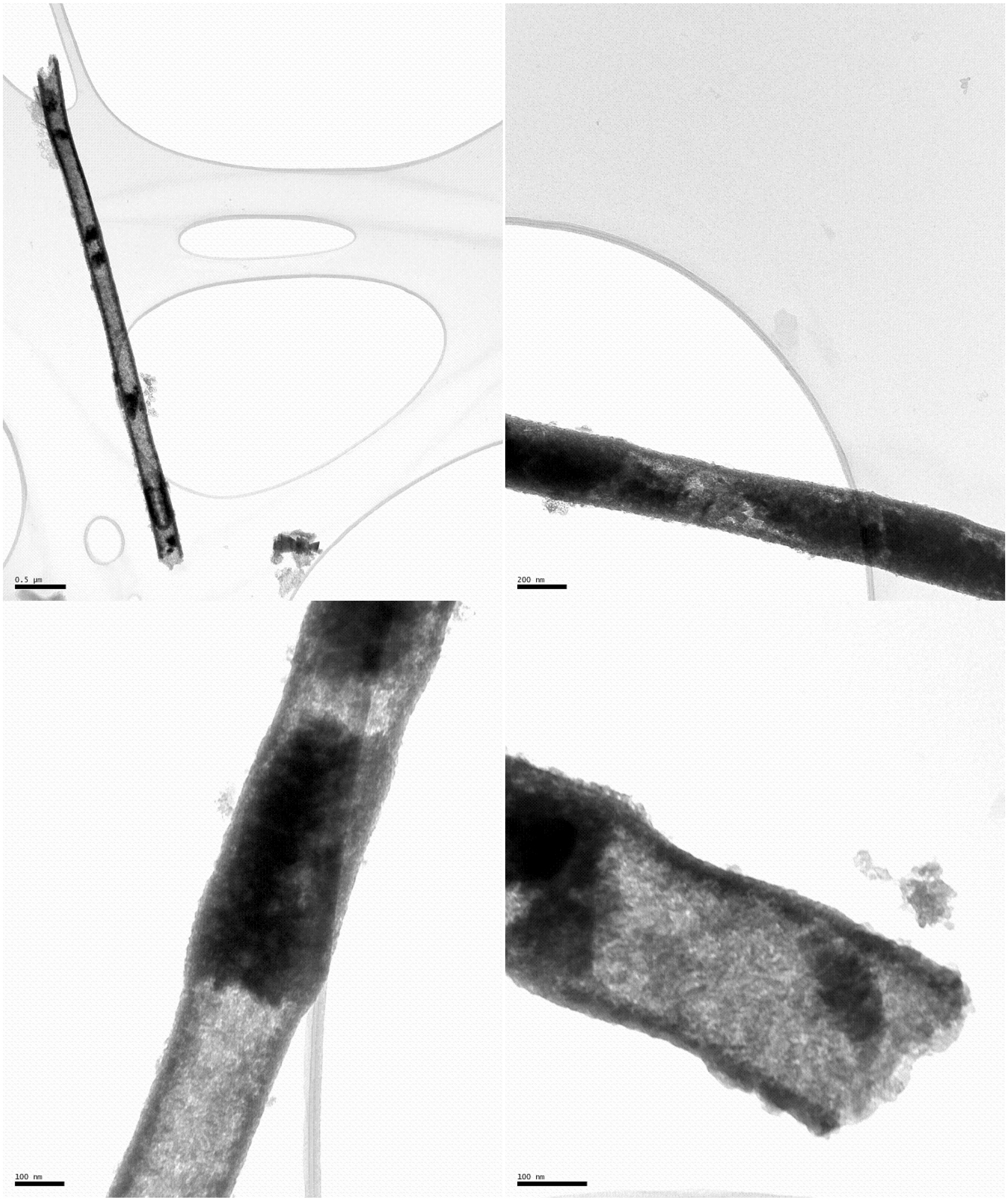
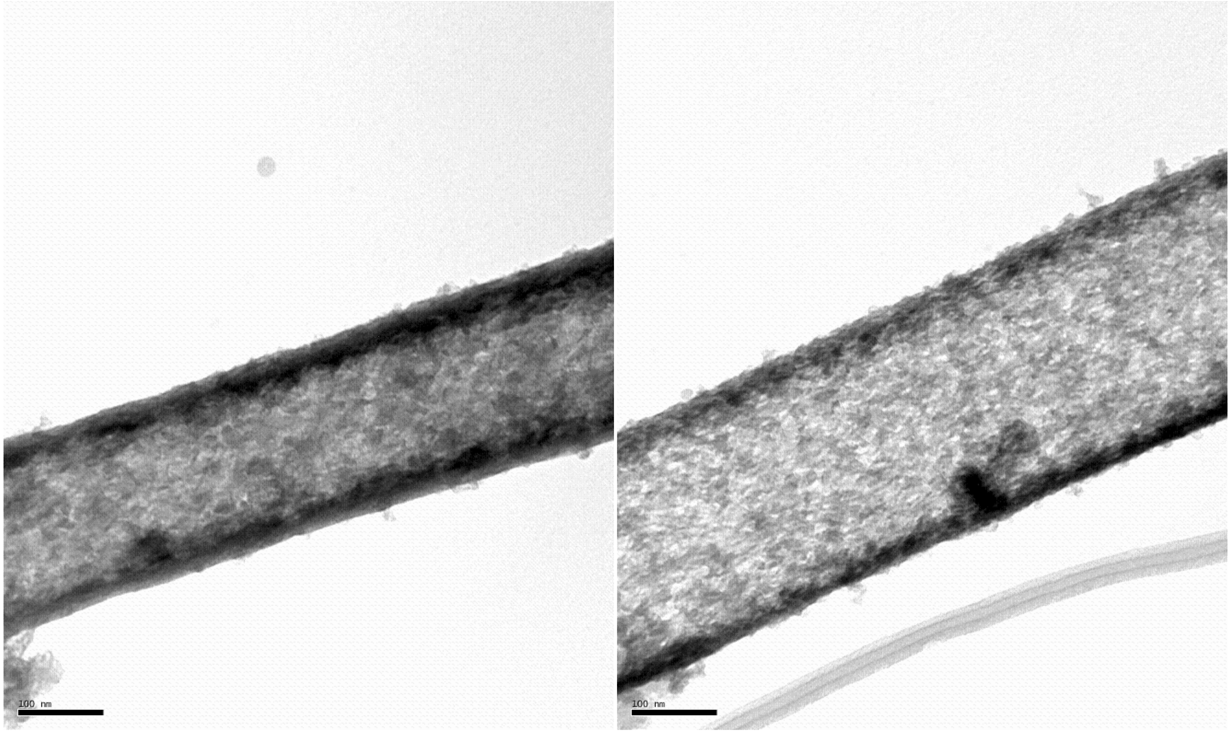
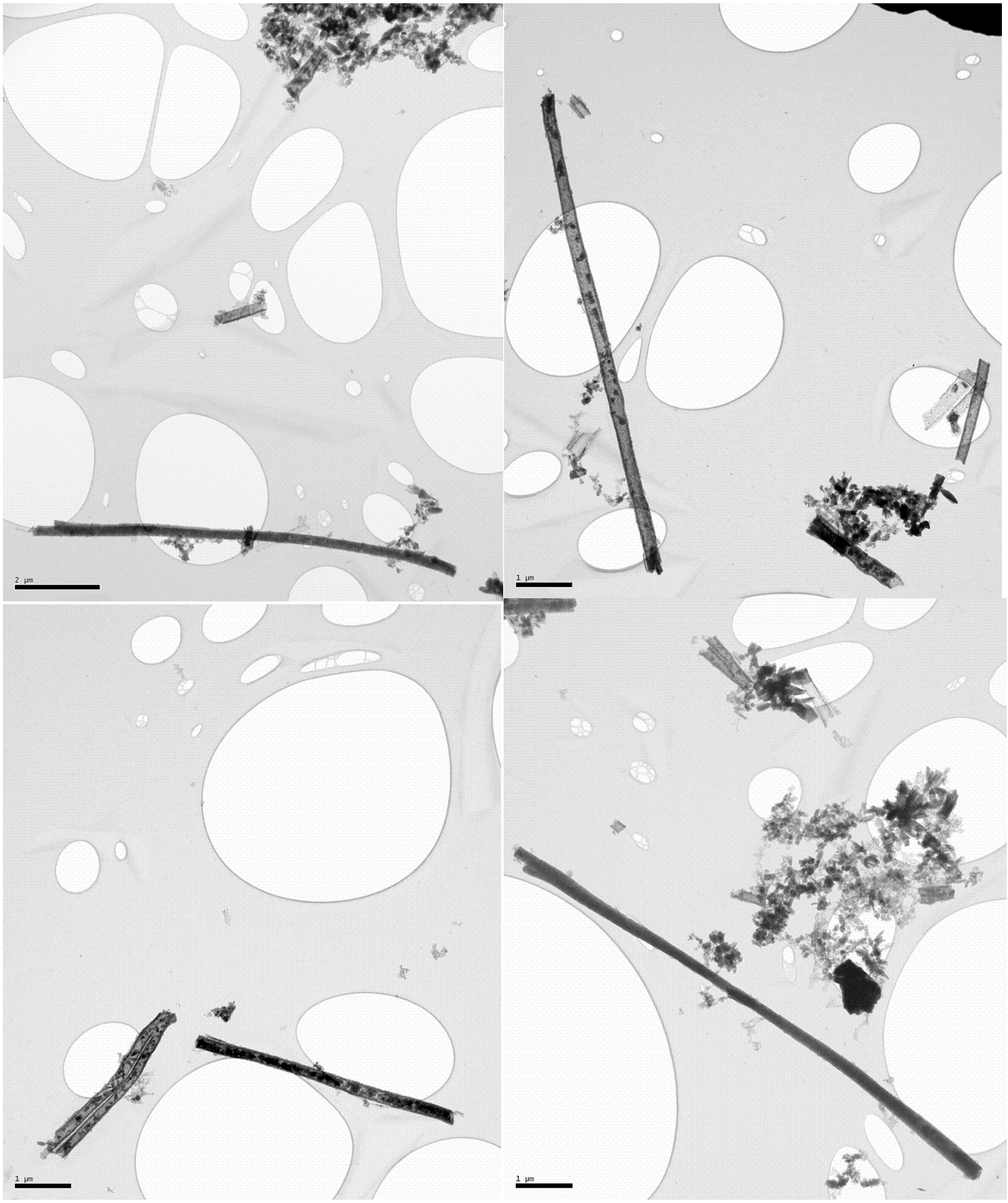
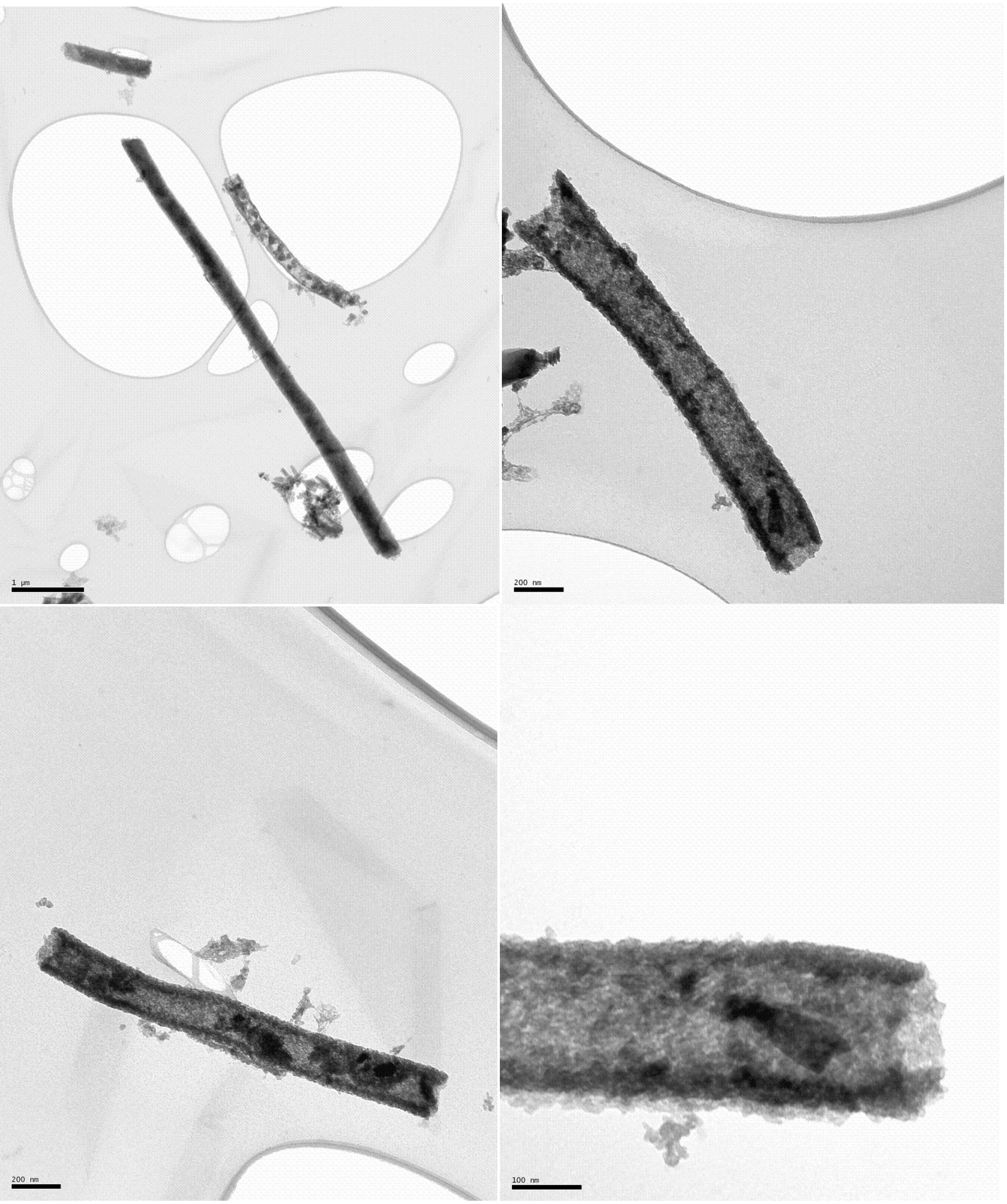
0.5 μm
0.5 μm
0.5 μm


0.5 µm
200 nm
100 nm
100 nm


100 nm
100 nm

13.3 TEM Images of 4-layer PMMA at 150C

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200 nm
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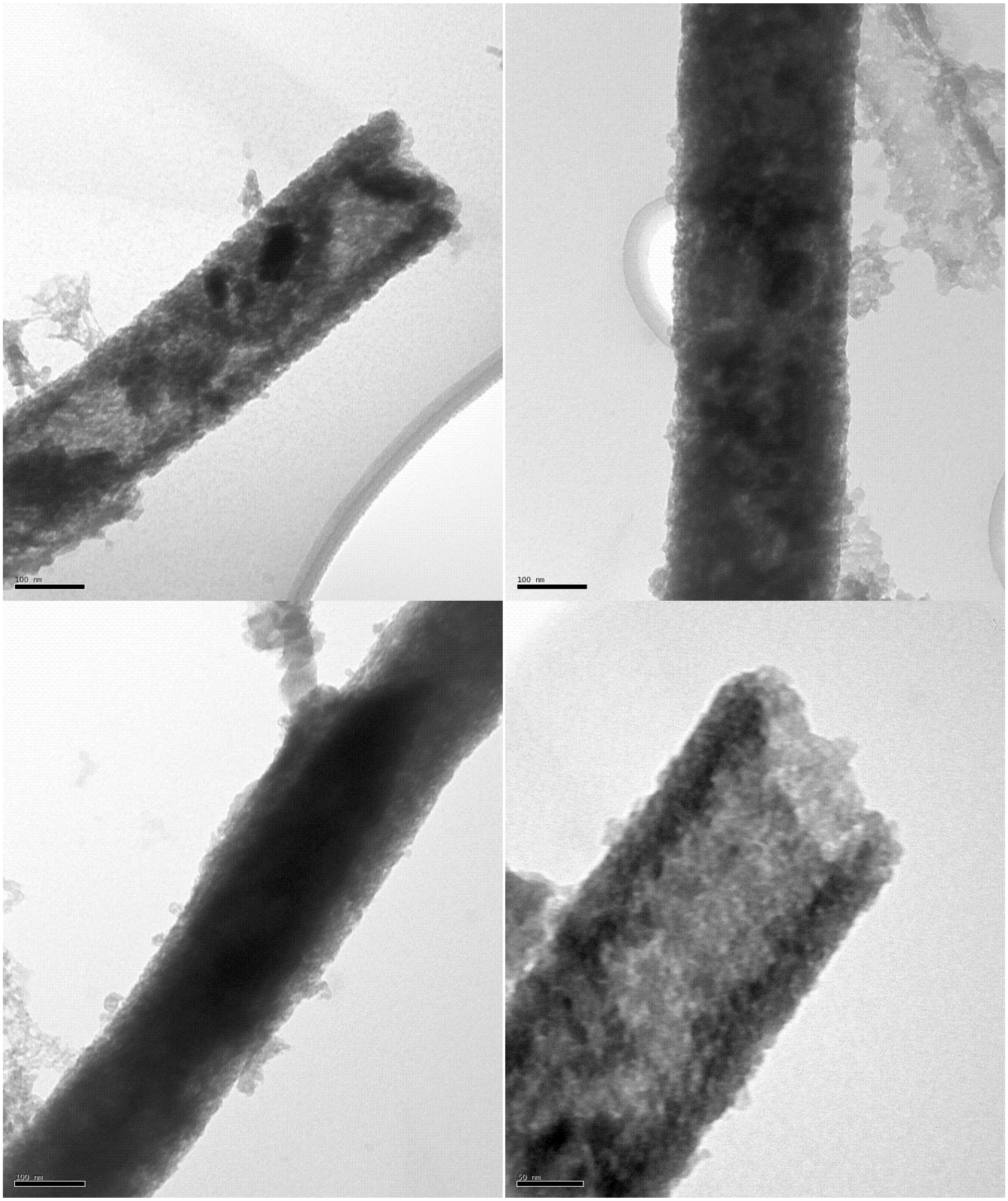
100 nm
100 nm
100 nm
50 nm