# Mechanism of Nanostructure Formation during Solution Template Wetting

By Meghan A. Pasquali

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**Approved:**_____

Richard D. Sisson, Jr., George F. Fuller Professor,

Director Manufacturing & Materials Science & Engineering

Co-Advisor:_____          Co-Advisor:_____

Jianyu Liang, Assistant Professor                Satya Shivkumar, Professor

Mechanical Engineering                               Mechanical Engineering

# ABSTRACT

Biomedical research has shown that one-dimensional nanostructures present many potential advantages as delivery vehicles for drugs and biologics. These elongated structures have high aspect ratios that enable increased drug loading capacities and have been shown to have longer *in vivo* circulation times than other spherical nanoparticles. The increasing interest in these one-dimensional structures has necessitated the developments of fabrication methods for the precise control of the final morphology. A simple, cost effective means of producing nanotubes and nanorods is known as solution template wetting. While this technique has been used to fabricate many different types of elongated nanostructures, the parameters governing the final morphology remain ambiguous. The objectives of this research are to investigate these critical parameters, and furthermore to develop an understanding of the physical mechanism of nanostructure formation. The effects of the infiltration technique, dipping time, polymer molecular weight and template pore size on the morphology of the resulting nanostructure have been evaluated. Key results have established that the infiltration technique is a critical parameter that can enable the formation of stable nanotubes at very low polymer concentrations. Additionally, a tube to rod transition occurs as the infiltration time is increased over 18 hr. An investigation of the rheological properties of high and low molecular weight solutions also indicates that the capillary flow and infiltration of polymer occurs differently. Finally, the pore size was also shown to affect the ability to form hollow, stable structures, and that relatively large pore sizes are necessary for nanotube formation. The culmination of these results is an understanding of the physical layering mechanism of structure formation, and the tube to rod transition can thus be predicted by researchers investigating the use of elongated nanostructures for biomedical applications.

# ACKNOWLEDGEMENTS

I would like to thank the numerous people who have helped me throughout my graduate studies at Worcester Polytechnic Institute. First, my advisors have been more than generous in their willingness to help me learn and develop my research skills. Professor Shivkumar has been a wonderful resource throughout my education for information on materials of all sorts; not only metals, ceramics and polymers, but also one of his favorites, food. He has pushed me to achieve as much as possible, and been a great professor to work with as a teaching assistant. I would also like to thank Professor Liang for her continual support and assistance throughout this project. She has guided me with her vast knowledge of nanomaterials and been a kind mentor.

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# CHAPTER 1: INTRODUCTION

The National Nanotechnology Initiative (NNI) was a federal program developed by the United States government to promote the innovation and research of new nanotechnology; or materials that are between 1-100 nm in size [1]. The program began in 2001, and consists of 25 federal agencies that financially support the development of new nanomaterials. Since its launch, nanomaterials have been developed for energy storage [2], material enforcement [3], computational devices [4] and medical diagnostic and therapeutic agents [5], among many more. The National Institutes of Health (NIH) and National Science Foundation (NSF) are two organizations that specifically sponsor research for biological applications of nanoparticles [1]. Such applications may include the development of nanoparticles for carriers of drugs and biologics [6], imaging of tissue and small organelles [7], and advancing genomic research [8]. The success of using nanoparticles for these *in vivo* applications will rely heavily on the ability to fabricate materials with specific morphologies.

It is known that the architecture of a nanomaterial introduced into the body will affect its behavior *in vivo* [8]. One structure that has been heavily researched for numerous biomedical applications is the carbon nanotube. Discovered in 1991 by Ijima, the carbon nanotube has many structural advantages over other spherical nanoparticles [9]. The nano-architecture is unique because it has a very small diameter (within the nanometer range), however a length that is much larger, reaching microns or even millimeters [9]. For delivery of drugs and biologics, this is advantageous because high drug loading capacities can be achieved. Additionally, the increased surface area allows for conjugation of molecules on the surface of the structure [8]. However, the inherent toxicity of carbon nanotubes is a major obstacle that researchers must overcome before these nanostructures can be used *in vivo*. As an alternative, researchers are investigating

polymeric materials due to the many physical advantages they offer. Some polymers can biodegrade, while others can be made porous, be co-polymerized, and even exhibit smart behavior. These properties can be combined to enhance the efficient cell penetration and delivery of biologics. Finally, nanotubes have been shown to exhibit long circulation times within the body because they are difficult for the macrophages, the body's main defense mechanism, to eradicate [5]. Although the use of elongated nanostructures for biomedical applications seems promising, one of the greatest challenges in nanotechnology, controlled and uniform fabrication, must first be overcome.

One of the simplest and cost effective means of fabricating elongated polymer nanostructures is known as the template wetting method [10]. This technique can be used to produce uniform, elongated polymer structures from either polymer melts or polymer solutions. During the fabrication procedure, a nanoporous template typically made of anodized aluminum oxide (AAO), is filled with a polymer melt or solution. Once the polymer is deposited on the pore walls and fully dried, the template can be dissolved away to release the nanostructures. While this method can be used to produce highly uniform structures, the fundamental mechanism of nanostructure formation is relatively unknown. Solution template wetting, the main focus of this research, is controlled by various parameters including the polymer concentration and molecular weight [11], solvent [12], and infiltration technique [13]. However, the role that each of these factors plays in determining the final morphology of the nanostructures remains ambiguous. Biomedical applications require that the nano-architecture be highly uniform, and thus a thorough understanding of the parameters governing structure formation is necessary before solution template wetting can be used to fabricate structures for medical research.

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# CHAPTER 2: RESEARCH OBJECTIVE

The objective of this research was to develop a fundamental understanding of the mechanism of nanostructure formation during solution template wetting and was achieved through an investigation of the critical parameters that govern the tube to rod transition.

- The effect of the infiltration technique was studied to determine if there was an effect on resulting nanostructure morphologies. A "multiple dipping" method was developed and compared to a traditional "single immersion" technique used by most research groups.

- The single infiltration time was varied to determine if this affected the final nano-architecture and additionally could piece together inconsistent published results.

- The polymer molecular weight was varied above and below the entanglement molecular weight to identify differences in resulting structures. The effects of polymer chain entanglements were used to validate the respective rheological properties of high and low molecular weight solutions.

- The wetting behavior of polymer solutions was studied by measuring the contact angles on nanoporous templates.

- The template pore sizes were varied to determine if there was any effect on the final nanostructure morphology.

# CHAPTER 3: RESEARCH PLAN

This work is a compilation of the various papers that have been submitted or are being submitted for publication in journals and conference proceedings.

1. Mapping of Polymer Nanostructures Using Template Assisted Method, *ANTEC 2010 Conference Proceedings*

2. Role of template and infiltration technique on resulting morphology of polymer nanostructures, *Materials Letters*

3. Effects of Time and Template Pore Size on the Morphology of Polymer Nanostructures Formed with the Template Assisted Method, *ANTEC 2011 Conference Proceedings*

4. Role of Template Filling Techniques on Polymer Structure during the Production of Nanoparticles, *Current Paper*

MAPPING OF POYLMER NANOSTRUCTURES USING TEMPLATE ASSISTED METHOD

*M. Pasquali[1], J. Liang[2], S. Shivkumar[2]*
*Department of Materials Science and Engineering, Worcester Polytechnic Institute*
*100 Institute Rd. Worcester, Ma 01609*

**Abstract**

Recently it has been shown that the morphology of nanotubes plays a critical role in determining their behavior *in* vivo. The purpose of the current work is to utilize anodized aluminum oxide (AAO) templates to fabricate polystyrene nanostructures. The effects of molecular weight, concentration, template pore size and solvent on the resulting morphology have been characterized. Results indicate complete filling of homemade templates was achieved with 1wt% polymer solutions of when $M_n > M_e$.

**I. Introduction**

Nano-biotechnology is an emerging field due to the potential applications of nanomaterials as carriers for drugs and biological molecules, as well as imaging agents [1]. The properties of the nanoparticles can be tailored such that they have a specific size, composition, architecture, and surface chemistry, with the shape being one of the most important features to dictate the particle's behavior *in vivo*. Nanotubes and nanorods are elongated structures with large aspect ratios that enable them to have a high loading capacity [2]. Additionally, the filamentous structure has been shown to have longer blood circulation times than spherical architectures, partly due to the ability to escape attack by the body's immune cells [3]. For these reasons, nanotubes and nanorods are being studied extensively for their potential in drug delivery applications.

A common procedure to synthesize nanotubes and nanorods is the use of a porous, anodized aluminum oxide template (AAO) that can be infiltrated with a polymer solution or polymer melt [4]. Once the solvent has evaporated or the polymer melt solidified, the AAO template can be dissolved away leaving behind the polymer tubes or rods. Wendorff et al.

studied the effects of molecular weight, solvent conditions, and concentration of polymer on the resulting morphologies of polystyrene nanorods/nanotubes fabricated from commercial templates [5]. They found that the type of solvent and concentration are important factors in the formation of cylindrical nanoparticles, while the molecular weight dictates the type of particle, i.e. tube or wire [5]. Other researchers have shown that the resulting morphology through template wetting is highly dependent on the solvent-polymer interactions [6]. These groups have shown the effects of different parameters on the resulting nano-morphologies, however have not addressed the effects due to the template. It is well known that commercial templates have large pore sizes that are not uniform. While the effects of the in-homogeneities are unknown, they can potentially be eliminated through the use of a homemade template. Homemade templates can be fabricated with small pore sizes that are highly uniform. The purpose of this work is to utilize these templates during the characterization of polystyrene nanotubes and nanorods fabricated under varying conditions. Parameters including the molecular weight and infiltration technique have been varied to begin mapping the resulting morphologies. Ongoing research will examine the additional effects of varying the polymer concentration, template pore size, and solvent.

## II. Experimental

### Materials

Polystyrene (PS) ($M_n$=170,000 g/mol, polydispersity index= 2.06) was purchased from Sigma Aldrich, while PS ($M_n$=18,100 g/mol, and $M_n$=973,000 g/mol, with polydispersity indexes=1.07) were purchased from Scientific Polymer Products. Tetrahydrofuran (THF, ACS reagent, >99.0%) was purchased from Sigma Aldrich and used as is. Aluminum sheets used in

the preparation of templates were purchased from Electronic Space Products International.

**Procedures**

An anodization technique described previously [3] was used to prepare the AAO templates. Initially, the aluminum samples were electrochemically polished in perchloric acid at 0°C and 15V DC for 4 min. Then the samples were coated with nail polish (on the back side) and adhered to Teflon tape. The first anodization was carried out at 40V DC for 16 hrs and 10°C. Following this step, the aluminum samples were submerged in chromic acid for 2 hrs. The templates were then anodized a second time in oxalic acid for 18 hrs. The AAO membrane was separated from the aluminum substrate by soaking in $HgCl_2$ solution for 1.5 hrs. Finally, the barrier layer was removed by soaking the samples in .1M $H_3PO_4$ for 4.5 hrs.

AAO templates were infiltrated by solution wetting. Three solutions were prepared with 1 wt% PS ($M_n$=18,100 g/mol, $M_n$=170,000 g/mol, and $M_n$=973,000 g/mol) in THF. Droplets of the solution were placed on a glass cover slide, and the top surface of the template was dipped 1, 2, 3, or 4 times in an attempt to achieve complete filling with the polymer solution. Once the solution had completely evaporated, the AAO templates were etched and dissolved in .1M NaOH. All samples were characterized with JSM7000 SEM to observe the surface characteristics and morphology.

**III. Results and Discussion**

**Template Characterization**

The homemade template produced from the first anodization procedure is shown in Figure 1a. It consists of pores ranging from 50-60 nm in diameter, with densities on the order of

$10^{10}$ /cm$^2$.  The SEM image also shows that the pores are uniform with a hexagonal pattern on the surface.   The top surface of a typical commercial template is shown in Figure 1b for comparison.  In the commercial sample, the pore diameters vary appreciably, from 10-500 nm; additionally the pores are not uniform.

A comparison of the cross sectional views of the templates with pore diameters of 50-60 nm and the commercial template is shown in Figure 2.  The homemade template has a much smoother texture than the commercial template while the cross section of the commercial template shows inner voids and irregular patterns.   These irregularities cannot be controlled and thus may have an undesirable impact on the final nanostructures.   Homemade templates eliminate these defects and provide better control over the morphologies of nanorods and nanotubes synthesized with the solution wetting technique.

The pore diameter of the template is critical because it controls the properties of the final structure.   The techniques developed in this study enable the production of templates with controlled pore characteristics.   Hence, nanotubes and nanorods of the desired size may be produced in order to dictate appropriate *in vivo* behavior [3].

**Infiltration Effects**

A technique based on capillary action was used to fill the pores in the template.  Capillary forces rely on polymer-solvent interactions, in addition to interfacial reactions with the template walls [6].  As a result the solution is able to fill the pores, leaving polymer behind upon solvent evaporation.   The templates with pore diameters of 50-60nm were completely filled after 3 infiltrations with 1wt% PS ($M_n$=170,000 g/mol) solutions.  Cross sectional views of the polymer rods are shown in the SEM images in Figure 3.   It can be observed that the rods are nucleating

from the top surface and have completely filled the template all the way to the bottom surface (thickness of template = 60µm). Electron diffraction confirmed that the polymer filled the entire length of the template. The diameter of the rods is essentially equal to the pore diameter indicating the rods exhibited very little shrinkage. A thin polymer film can be seen at both the top and bottom surfaces, which may have resulted from an excess of solution that accumulates on the surface.

These results are in direct contrast to the data presented by Wendorff et al. [5]. Their results indicate that at concentrations of 3 wt% PS, the structures completely collapsed, and at 7 wt% the structures were partially collapsed [5]. They recommend a concentration of at least 10 wt% PS in order to produce stable nanorods [5]. The present investigation indicates that even 1wt% PS can completely fill the AAO template and form stable polymer nanorods. The differences may be attributed to the use of a theta solvent by Wendorff et al. (DCM) and a good solvent (THF) in this investigation. The infiltration process may also contribute to the observed differences. While Wendorff et al. soaked the template for 1 hour to infiltrate the pores, in this study the templates were dipped in the solution for 10 sec, removed and held for 10 sec. This process was repeated three times. Additionally, the homemade templates used in this investigation have smooth inner surfaces that maximize the polymer interactions with the template wall, whereas the other researchers used commercial templates.

**Effects of Molecular Weight**

Two extreme molecular weights, below ($M_n$=18,100 g/mol) and above ($M_n$=973,000 g/mol) the entanglement molecular weight ($M_e$=130,000 g/mol) were used to determine the effects on the resulting nanostructures. The structures resulting from the low molecular weight

PS are shown in Figure 4a. It appears that the polymer did not completely fill the template, most likely due to the low molecular weight and inability of the polymer to adhere to the template wall. It is also possible that the pores were completely filled with the solution initially, and the structure collapsed after solvent evaporation. The structures resulting from the high molecular weight PS are shown in Figure 4b. In this case stable nanostructures were produced. Further, the data suggest nanotube morphologies were formed.

The effects of molecular weight are consistent with the results obtained by Wendorff et al [5]. In the present study, when $M_n < M_e$, PS did not form the stable, elongated structures that were typically obtained at $M_n > M_e$. Feng and Jin were able to produce PS nanorods with THF as a solvent for molecular weights ranging from 5,200 g/mol to 650,000 g/mol [6]. The present investigation suggests that stable rod or tube structures can be formed only when $M_n > M_e$. It is well known that in polymer solutions, the effects of entanglement become significant at Be >1 [7]. Be values for the various conditions used in this study were estimated to be 0.13 ($M_n$=18,100 g/mol), 1 ($M_n$=170,000 g/mol) and 2 ($M_n$=973,000 g/mol). Stable nanostructures were observed for Be numbers > 1. Consequently, the effects of entanglement are significant in producing stable nanostructures.

## IV. Conclusions

Solution wetting has proven to be an effective means to prepare nanostructures from porous AAO templates. Commercial templates have generally been used to produce the nanostructures. The commercial templates contain a wide pore distribution and the inner surface walls may contain irregularities. A technique to produce homogenous templates was developed and used to fabricate various nanostructures from PS. Homemade templates provide uniform

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pores to better control the morphologies of the resulting nanostructures.

The results achieved from these preliminary experiments show that nanorods can be formed from 1wt% concentrations of PS in homemade AAO templates. By varying the infiltration technique, complete filling was achieved even at this low concentration. The resulting structures were rod-like with a uniform diameter and elongated length, ideal for cell penetration in numerous drug delivery applications. It was also observed that stable nanostructures were generally produced when $M_n > M_e$.

Other parameters such as the solvent, template pore size, and concentration are currently being studied for their contributions on the resulting morphology of the nanostructures.

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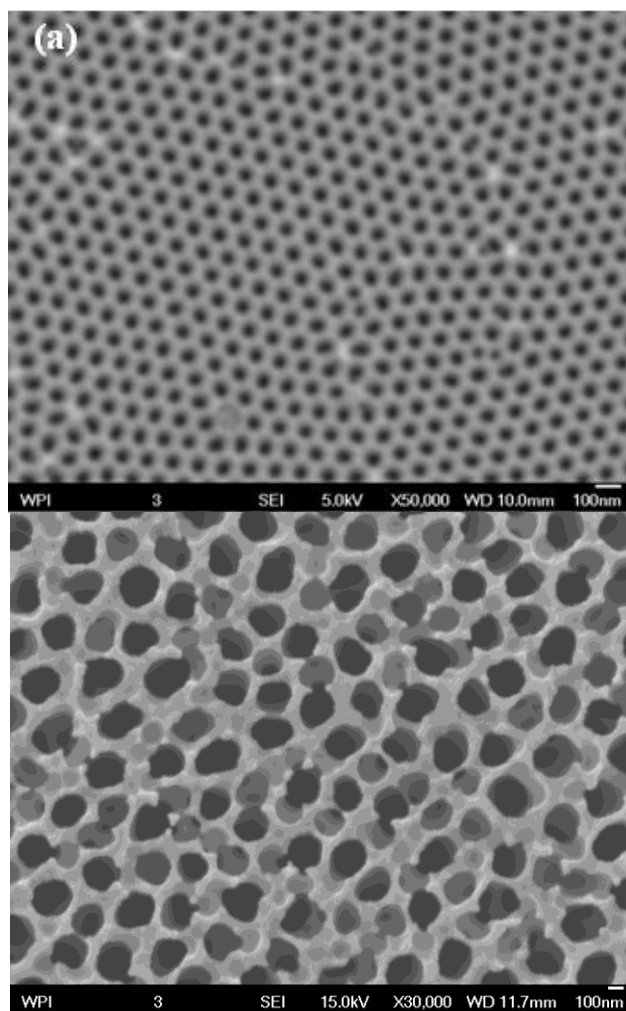
**Figure 1: SEM images of AAO templates comparing the uniform pore size achieved in (a) 50-60nm pore diameter, to the non-uniform pore sizes in (b) commercial templates**
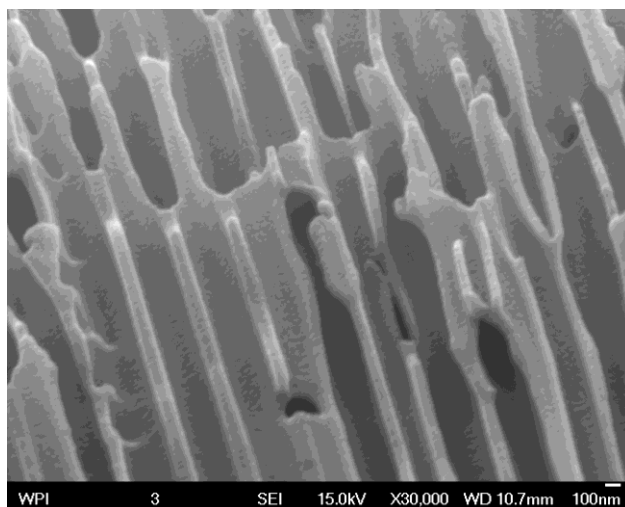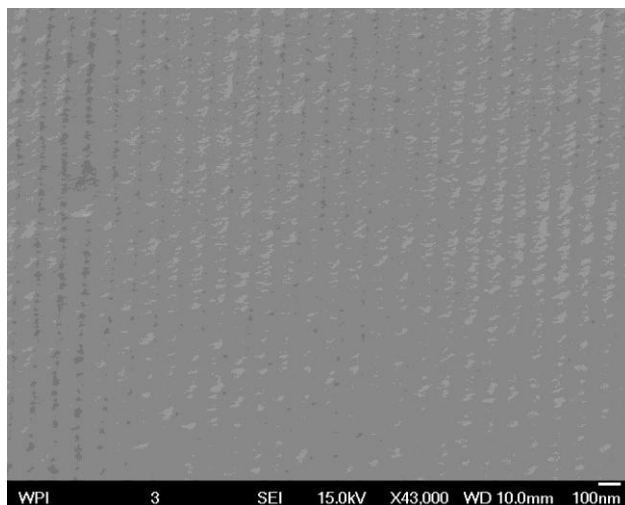
**Figure 2: Cross-sections of AAO templates (top) 50-60nm pore diameter with smooth inner walls, (bottom) commercial template showing irregular patterns and voids**
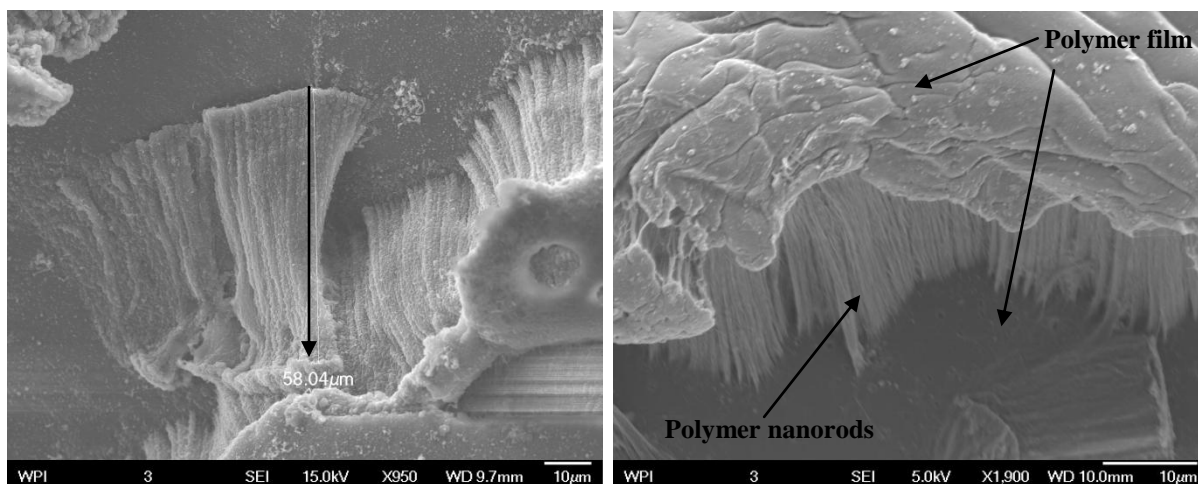
**Figure 3: SEM images showing stable 1wt% PS nanorods formed between two polymer films. (left) stable nanorods have completely filled the template, (right) nanorods can be seen between the polymer films at the top and bottom surfaces. Note that the polymer nanorods have completely filled the template, ~60μm thick.**
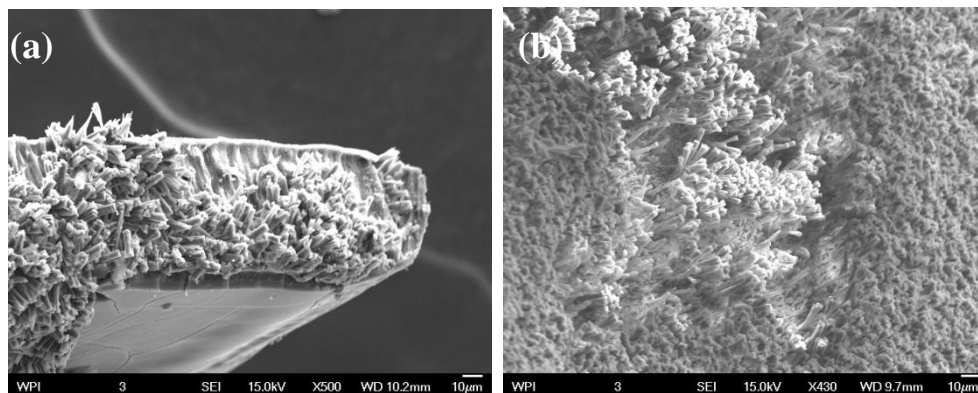


**Figure 4: Photographs showing 1wt% PS nanostructures after the template was etched. (a) C=1 wt% , $M_n$=18,100g/mol which are truncated and have not filled the template completely, (b) C=1 wt%, $M_n$=973,000g/mol which are elongated, tube structures**

**Role of Template and Infiltration Technique on**
**Resulting Morphology of Polymer Nanostructures**

Meghan Pasquali[1], Jianyu Liang[2], Satya Shivkumar[2]
*Worcester Polytechnic Institute*
*Department of Materials Science and Engineering*
*100 Institute Rd, Worcester, Ma 01609*
mpasqual@wpi.edu   jianyul@wpi.edu   shivkuma@wpi.edu

**Abstract**

Polymer nanotubes are commonly fabricated using the template assisted method. In the present study, polystyrene nanotubes were formed through a unique dipping technique that has not previously been reported. Anodized aluminum (AAO) templates were synthesized and infiltrated with polystyrene-tetrahydrofuran solutions. The effects of the template, polymer molecular weight and concentration on the final morphology were examined. The results indicate that stable nanotubes can be formed in homemade and commercial templates with polymer concentrations as low as 0.5 wt%. Nanotubes also resulted from a range of molecular weights indicating that the infiltration technique may be the primary factor enabling the formation of hollow structures.

**1. Introduction**

The template assisted method is a common technique used to fabricate polymer nanostructures [1]. Porous templates, typically made of silicon or anodized aluminum (AAO), are infiltrated with either a polymer melt or solution [2, 3]. The morphology of the resulting structures depends on numerous variables including the polymer molecular weight and concentration, the surface characteristics of the template, and the wetting properties at the

interface [3-5]. Polystyrene (PS) is one of the common materials used to study the effects of these process variables on the final polymer morphology [6]. It has been shown that PS can be exploited with the template assisted method to form elongated nanostructures, including nanorods and nanotubes [4, 5]. Initial results suggested that the morphology of the structures can be tailored by controlling primary solution parameters such as polymer molecular weight, concentration and solvent properties [4]. However, additional reports conclude that the molecular weight and concentration may have little impact on the final nanostructures, and rather that the interaction between the solvent and the template is dominant in determining morphology [5]. Dougherty and Liang [7] also suggest that nanostructures fabricated in commercial templates differ from those formed in homemade templates. While most published work utilizes commercial templates, there remains uncertainty regarding the potential effects of the nature of the template on the polymer structures. This study examines the influence of polymer molecular weight and concentration in the fabrication of nanotubes, using both commercial and homemade templates. Furthermore, the effects of wetting technique on the morphology of the final nanostructures were also investigated.

## 2. Experimental

Polystyrene ($M_n$=170,000 g/mol, polydispersity index= 2.06) and Tetrahydrofuran (THF, ACS reagent, >99%) were purchased from Sigma Aldrich. PS ($M_n$=18,100 g/mol, and $M_n$=973,000 g/mol, polydispersity index=1.07) was purchased from Scientific Polymer Products, New York, NY. Studies examining the effects of wetting technique utilized *Anodisc* commercial templates purchased from Whatman.

An anodization technique described previously was used to prepare the homemade AAO templates [8]. The aluminum samples were anodized twice in oxalic acid and the AAO membrane was separated from the aluminum substrate following submersion in mercury chloride. Pieces from commercial and homemade templates were obtained for microscopic examination.

AAO templates were infiltrated with polymer solutions of varying concentrations (1 wt%, 0.5 wt%, and 0.25 wt% PS in THF) prepared at room temperature. Templates were first dipped in each solution with the top surface faced downward. After 10 s, templates were removed from the solution and positioned with the top surface facing upward. Following another 10 s exposure to ambient conditions, the same procedure of dipping and extraction was repeated. A total of three such cycles was performed to obtain a total dipping time of 30 s, interspersed with two (10 s) drying periods. All samples were dried in air for at least 24 h following the dipping procedure. A small portion of each template was sectioned from the ends for characterization with JSM7000 Scanning Electron Microscope (SEM). Polymer filled templates were dissolved in 0.1 M NaOH for at least 36 hr before examination with JEOL 100CX Transmission Electron Microscope (TEM).

## 3. Results and Discussion

Homemade AAO templates (60 μm thickness) fabricated with the two step anodization procedure contained evenly distributed pores with diameters of 50-60 nm (Fig. 1). The anodization time and temperature can be used to control the template thickness and pore diameter respectively [7]. Manipulation of these parameters allows for control of the size and

uniformity of the resulting nanostructures. Homemade templates also yielded an internal pore surface that was smooth and free of both pits and voids. Consequently, the surface of the polymer nanostructures was uniform and generally did not contain visible defects. By comparison, templates purchased commercially have a broad distribution of pore sizes, with diameters ranging from 20-300 nm. Additionally, the inner walls of these templates contain voids that may affect the nucleation and growth of the polymer at the cell walls, thereby preventing the formation of a smooth and uniform surface. Note the surface defect in Fig.1 (b).
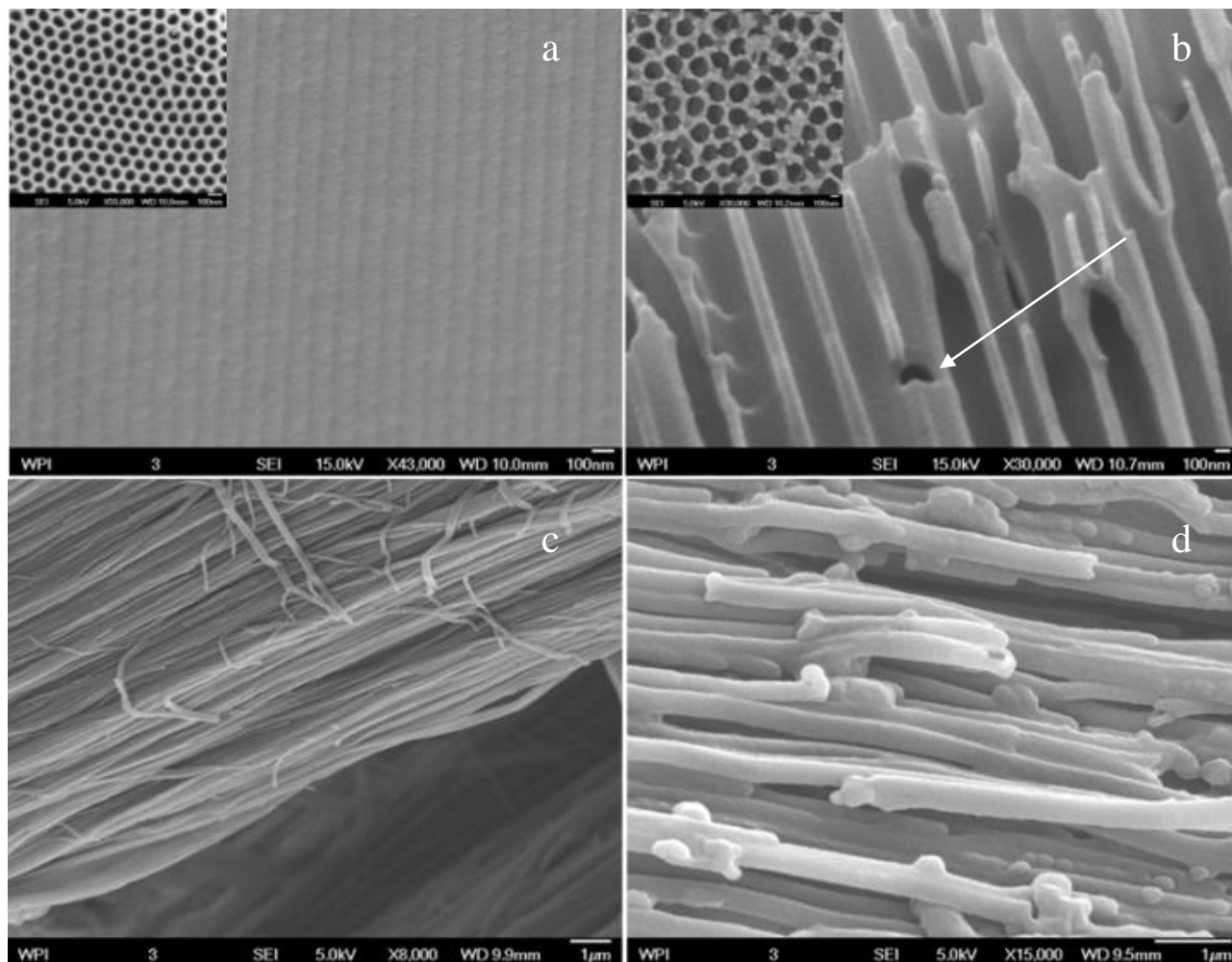
**Fig. 5: Comparison of homemade and commercial templates and the corresponding polymer nanostructures. (a) Cross-sectional view of homemade template with smooth inner walls. Inset shows the top surface with uniform pore size and distribution. (b) Cross-sectional view of commercial template showing voids within template walls. Arrow indicates a hole along the inner surface. Inset shows non-uniform pores. Nanostructures formed in (c) homemade templates, with smooth outer surfaces, (d) commercial templates showing defects.**

The infiltration technique used in this study is different from those previously described. With the sequential dipping method, nanotubes were formed at concentrations of 1 wt% PS, with a range of molecular weights ($M_n$=18,100 g/mol, $M_n$=170,000 g/mol, and $M_n$=973,000 g/mol). In addition to forming tube-like structures, it was found that the polymer completely filled the template as shown in Fig. 2. Schlitt *et al.* indicate that the polymer molecular weight and concentration, as well as the type of solvent may have a significant impact on the morphology of nanostructures formed with the template assisted method [4]. The documented technique was an immersion process during which commercial templates were soaked in PS polymer solutions for 1hr or the solution was dropped onto the template sequentially [4]. Results from their study suggest that good solvents and concentrations of greater than 10 wt% polymer are necessary for stable structures to form [4]. Additionally, they report that nanorods are formed at molecular weights below 7,000 g/mol, while rods with periodic voids form at molecular weights between 17,000 and 75,000 g/mol, and nanotubes form at molecular weights greater than 75,000 g/mol [4].
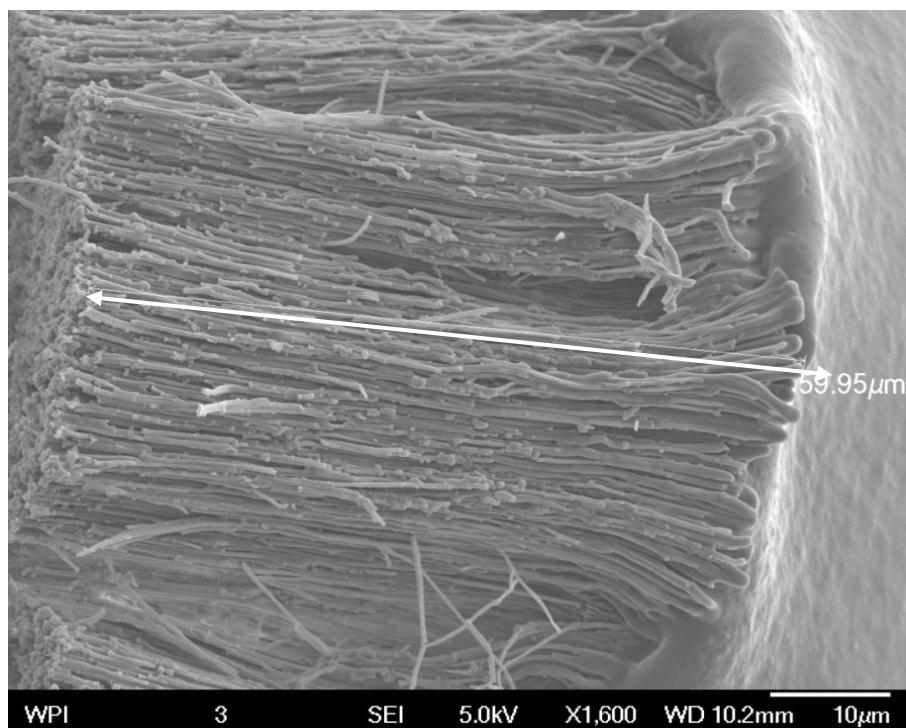
**Fig. 6: Micrograph showing the structure of the filled polymer after the template was fractured by a simple bending action. (1 wt% PS, $M_n$=18,100 g/mol, commercial AAO template with 60μm thickness)**

Feng and Jin showed that PS nanorods can be formed with the template assisted method for molecular weights ranging from 5,200 g/mol to 650,000 g/mol [5]. Their technique also involved an immersion process during which the templates were exposed to PS solutions for 24 hr [5]. The data indicate, however, that at low concentrations of PS (typically about 20 to 40 mg/mL), the polymer was unable to completely fill the template, resulting in structures that consist of nanospheres and nanocapsules. Meanwhile, elongated tube-like structures can be formed at concentrations of 150 mg/mL [5]. The results from both studies are in direct contrast to the present investigation where a) the templates were completely filled with PS for molecular weights ranging from 18,100 g/mol to 973,000 g/mol, and b) nanotubes were formed at

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concentrations as low as 1 wt% PS for both low and high molecular weight polymer. These apparent differences may be a result of variations in the infiltration technique. When the templates are exposed to polymer solutions for extended periods of time, the polymer may concentrate within the pores to form solid structures. Additionally, at low concentrations, the polymer may be unable to infiltrate the entire depth of the template. With the present dipping procedure, the solution may coat the inner walls of the template (during the first 10 sec) and subsequently, the extraction of the template from the solution enables solvent evaporation. This loss of solvent facilitates the formation of a thin polymer skin on the walls of the substrate, which eventually produces a nanotube. Even at concentrations as low as 1 wt% polymer, elongated tubes were observed because the polymer was able to fill the entire length of the template. Furthermore, nanotubes were obtained in both commercial and homemade templates, suggesting that the infiltration technique could be the principal factor controlling stable tube or rod regimes for various molecular weights and concentrations. Additional experiments are being conducted to examine the effects of the dipping technique on the resulting nanostructures.

The effects of polymer concentration on the morphology of the nanostructure were examined further with dilute solutions (PS concentration < 1%). Fig. 3 shows that even at a concentration of 0.5 wt% PS, the final structure consists predominantly of nanotubes. However, when the concentration is reduced further to 0.25 wt% PS, segmented structures with solid and hollow portions were obtained (Fig. 3). At such low concentrations, the polymer skin that forms on the cell walls may not be strong enough to withstand the pressure established during the evaporation of the solvent, and as a result, the structure may collapse. Notice that the nanotube wall thickness decreases from approximately 45 nm to 30 nm as the concentration is lowered from 1 wt% to 0.5 wt% PS. The wall thicknesses are significantly less than those reported by

previous investigators.  Schlitt *et al* [4] have measured this thickness to be about 50-60% of the pore diameter (for concentrations of 5 wt% PS) and whereas in the present study, the walls are approximately 10-20% of the outer diameter.
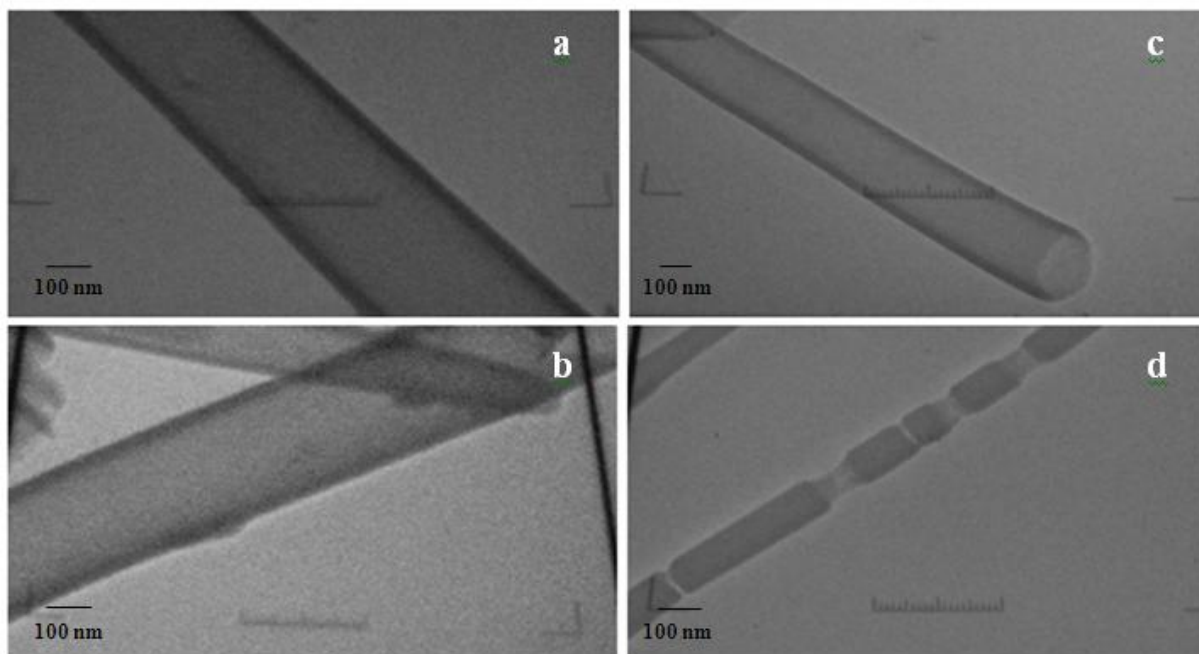


**Fig. 7: TEM images showing the effects of molecular weight and concentration on the resulting polymer nanostructures.  The outer diameter of all structures directly corresponds to the 200-300 nm pore diameters of the commercial templates.  Structures resulting from (a, b) 1 wt% PS ($M_n$=18,100 g/mol and $M_n$=973,000 g/mol respectively), (c) 0.5 wt% PS ($M_n$ =170,000 g/mol) nanotubes, (d) 0.25 wt% PS ($M_n$ =170,000 g/mol) segmented structures**

The ability to form nanotubes at very low polymer concentrations may be attributed to the processing technique used to infiltrate the templates.  The nanotubes were formed at concentrations well below the entanglement concentration ($C_e$) in the PS-THF system.  At $C_e$, there is a rapid increase in the viscosity of the solution due to the intertwining of polymer

molecules. This molecular entanglement may stabilize the polymer structure developing on the walls of the substrate to form hollow structures. For the PS-THF system, the product of $C_e$ and $M_n$ has been reported to be approximately 3 x $10^4$ [9]. From this value, $C_e$ can be calculated to be on the order of 0.18 g/mL for $M_n$=170,000 g/mol. Therefore it appears that stable nanotubes cannot be formed at the low concentrations used in this study. However, the removal of the substrate from the solution enables solvent evaporation, which effectively increases the polymer concentration in the solution to be greater than $C_e$. It is estimated that for a 1wt% PS-THF solution to attain $C_e$, at least 15 to 20% solvent evaporation must occur. The technique used in this study, with repeated dipping and extraction of the substrate, provided the necessary evaporation rate to stabilize a solid skin forming on the template walls. It should be noted that previous studies with the PS-THF system have not yielded hollow nanotubes at similar concentrations [5]. Feng and Jin formed nanostructures with an immersion technique that may have inhibited rapid solvent evaporation necessary for skin formation. Consequently, the resulting structures were typically solid nanospheres, capsules, and rods [5]. Furthermore, it has been reported that polymer concentrations as high as 10 wt% (0.1 g/mL) may be necessary to form stable nanotubes in the PS-cyclohexane system [4]. The evaporation rate of cyclohexane is lower than that of THF [10] and thus higher concentrations may be needed to stabilize the skin. In the current study, nanotubes were obtained for molecular weights ranging from 18,100 g/mol to 973,000 g/mol. Previous studies have shown that stable nanotubes can only be obtained at molecular weights greater than 75,000 g/mol (PS-dichloromethane) [4]. These results further confirm the importance of the infiltration technique in relation to solvent evaporation.

**4. Conclusions**

It has been shown that well established anodization techniques can be used to produce homemade templates with uniform pores on the order of 50-60 nm and with defect free internal surfaces. By comparison, commercial templates consist of a wide pore distribution (20-300 nm diameter) and may contain pits and voids on the internal surface. These apparent differences may impact the resulting nanostructure morphology. A modified infiltration technique was used to produce nanotubes at polymer concentrations as little as 0.5 wt%. Previous reports with PS have indicated that polymer concentrations as high as 10 wt% may be necessary to form stable nanotubes when an immersion infiltration technique is used. When the polymer concentration is below a critical value, stable nanotubes may collapse to form a fragmented structure. In the present study, nanotubes were formed for polymer molecular weights ranging from 18,100 g/mol to 973,000 g/mol (at concentrations of 1 and 0.5 wt% PS), indicating that the dipping technique may be the principal factor controlling the formation of stable nanotubes.

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# EFFECTS OF TIME AND TEMPLATE PORE SIZE ON THE MORPHOLOGY OF POLYMER NANOSTRUCTURES FORMED WITH THE TEMPLATE ASSISTED METHOD

*M. Pasquali[1], J. Liang[2], S. Shivkumar[2]*
*Department of Materials Science and Engineering, Worcester Polytechnic Institute*
*100 Institute Rd. Worcester, Ma 01609*

**Abstract**

The template assisted method is a simple, cost effective technique that can be used to fabricate polymer nanotubes. In this study, the solution wetting technique was used to form polystyrene elongated nanostructures in anodized aluminum oxide templates. The effects of time and template pore size were studied to determine the role each parameter plays in the final morphology. It was found that for PS solutions with high molecular weight polymer, hollow nanotubes can be formed for time periods <18 hr, whereas low molecular weight polymer forms solid nanorods. Additionally, relatively large pore diameters of ~200-300 nm are necessary to form nanotubes.

**Introduction**

Nanomaterials are gaining increasing interest within the biomedical industry for their potential advantages as drug delivery vehicles [1, 2], sensors [1, 3], tissue engineering scaffolds [4] and as imaging agents [5], among others. Nanotubes have a specific architecture that allows them to interact on a cellular level [6] and due to their elongated shape can effectively penetrate into cells [7, 8]. Polymer nanotubes in particular have potential *in vivo* applications because their properties can be controlled to manipulate the behavior and interactions within the body [9, 10].

Various fabrication techniques have been developed to produce polymer nanotubes. One simple, cost effective method relies on the use of a nanoporous template. This template wetting

technique can be performed using a polymer melt or solution that is infiltrated into the nanoporous substrate [11]. The deposition of polymer within the pore is driven mostly by capillary forces, with some, less significant gravitational effects [12]. Once the polymer hardens within the pores (during melt wetting) or the solvent evaporates, (during solution wetting) the template can be dissolved and the resulting nanostructures released. With this technique, various architectures can result, including nano-spheres, capsules, thin fibers, solid rods or hollow nanotubes [13]. For most drug delivery applications, it is highly desirable to achieve a hollow architecture that can be loaded with a therapeutic agent. Therefore, it is important to understand which parameters control the resulting morphology.

Fundamental research using the solution wetting technique utilizes polystyrene (PS) because it is a well characterized polymer. Some researchers suggest that high molecular weight polymer is necessary to form stable hollow structures [14] while others indicate that only solid nanorods can be formed with the solution wetting method, independent of molecular weight [13]. The concentration of polymer in solution wetting is another variable that must be considered. Previous research indicates that polymer nanotubes can be formed at concentrations as low as 1 wt% PS [15], while others have indicated that at least 10 wt% PS is necessary to form hollow structures [13, 14]. The ability to form hollow structures at very low concentrations may be affected by additional factors, including infiltration time and technique. Some researchers perform a single immersion for 1 or 24 hr [13, 14] while some research has focused on a multiple dipping technique. When this multiple dipping technique is used, a period of solvent evaporation occurs between each immersion. This may allow the polymer to harden along the inner walls of the nanopore such that a stable, hollow tube can ultimately be formed [15]. During a single immersion, there is no intermediate solvent evaporation, and thus it may be difficult to form

hollow structures if the substrate is immersed in the polymer solution for long periods of time. These differences in infiltration technique may have contributed to the contradictory results between researchers using 10wt% polymer as well as with the reported research using 1wt% polymer. The current study therefore aims to develop a model that can be used to describe the process of nanotube formation during the template wetting technique. In particular, the effects of time and template pore size have been investigated to determine the impact on the morphology of the resulting structures.

**Experimental**

**Materials**

PS with three different number average molecular weights ($M_n$=4,000 g/mol and PD=1.00, $M_n$=10,000 g/mol and PD=1.06, $M_n$=170,000 g/mol and PD=2.06,) and Tetrahydrofuran (THF), ACS were purchased from Sigma Aldrich. PS ($M_n$=18,100 g/mol and $M_n$=973,000 g/mol, PD=1.07) was purchased from Scientific Polymer Sciences, New York, NY. Aluminum sheets used to fabricate anodized aluminum oxide (AAO) templates were purchased from Electronic Space Products International. Commercial AAO *Anodisc* templates were purchased from Whatman.

**Methods**

The method used to fabricate homemade nanoporous templates has been described previously [16]. In short, aluminum sheets (1x5cm) were electrochemically polished in a percloric acid/ethanol mixture. The sheets were then anodized in 0.3 M oxalic acid to build a porous layer of aluminum oxide. The layer was then removed before anodizing a second time to form the final ordered and porous template. The resulting barrier layer was removed and the

pores were etched in phosphoric acid.

Polymer solutions were infiltrated into the AAO templates (either prepared or commercial) to form the nanostructures.  Solutions of 1 wt% PS (with varying molecular weights) in THF were infiltrated into the templates for various time periods (See Table1).  After a single immersion, the templates were allowed to dry in ambient conditions, (1 atm, still air, 25°C).  This procedure resulted in a thin polymer coating along the inner surfaces as well as on the top and bottom surfaces of the template.   The outer coating of polymer was etched in NaOH to separate the polymer structures from the AAO substrate.  Samples were characterized with a JSM 7000F Scanning Electron Microscope (SEM) and JEOL 100CX Transmission Electron Microscope (TEM). ImageJ Software was used to analyze the final structures.

**Table 1: Experimental design outlining the various molecular weights and infiltration times used**

| PS $M_n$ (g/mol) | Single Infiltration Time |
|---|---|
| 4,000 | 5 sec |
| | 10 sec |
| 10,000 | 30 sec |
| | 5 min |
| 18,100 | 30 min |
| | 1 hr |
| 170,000 | 6 hr |
| | 12 hr |
| 973,000 | 18 hr |
| | 24 hr |

## Results and Discussion

## Template Fabrication

A two step anodization procedure was used to fabricate highly uniform and ordered nanoporous templates. The first anodization formed a porous oxide layer that imprinted a hexagonal pattern on the aluminum substrate beneath. The patterned aluminum was necessary to direct the ordered growth of pores during the second anodization step. Following this step, the pores were widened in phosphoric acid. The results are shown in Figure 1. It can be seen that the pore sizes were typically 40-50 nm in diameter, and ~60 μm deep when anodized at 40 V. Additionally, they formed a regular, ordered pattern on the top surface. To create larger pore diameters, the voltage during each anodization was increased to 60 V. The resulting pore sizes of these templates were ~60-70 nm. Although the pore sizes were slightly larger, the ordered arrangement was interrupted. Commercial templates provided even larger pore diameters of ~200-300 nm, with little uniformity and no periodic arrangement. Figure 2 shows a comparison of the pore sizes in each template.
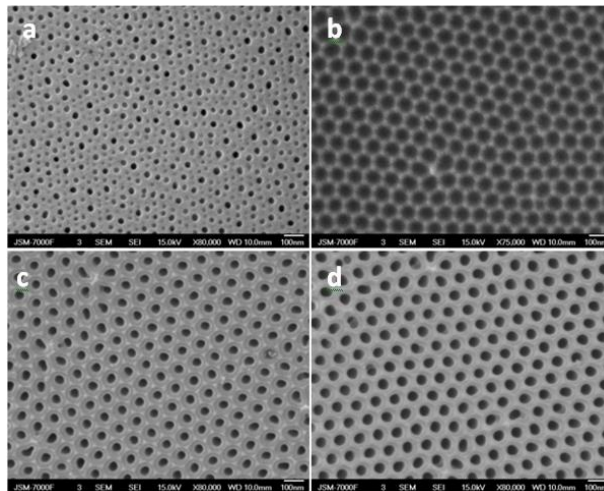
**Figure 8: Fabrication of AAO templates; a) random and non-uniform porous layer of aluminum oxide that forms after the first anodization, b) ordered hexagonal imprint that forms underneath the oxide layer, c) ordered and uniform porous aluminum oxide that forms after the second anodization, d) final AAO template after pore widening in phosphoric acid**
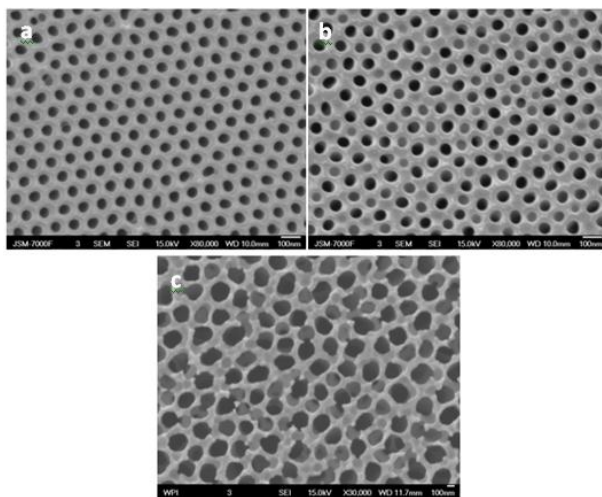


**Figure 9: Comparison of pore uniformity of final prepared and commercial templates; a) Homemade template anodized at 40 V, b) Homemade template anodized at 60 V, c) commercial template**

The ordered and periodic formation of prepared nanoporous templates is critical to form uniform nanostructures. Although larger pore sizes are available with commercial templates, they are neither periodic nor uniform such that the size of all resulting structures is the same. For *in vivo* applications, it is crucial that the size of the structures be identical because, as already mentioned, the size of the nanostructure affects its behavior. Efforts aimed at improving the anodization procedure to produce larger, uniform pore sizes are ongoing.

## Effect of Time

The solution template wetting method was used to fabricate PS nanostructures. The infiltration time directly corresponded to the wall thickness of the resulting structures. Short periods of time resulted in very thin walls, while longer periods of time lead to gradual wall thickening until solid nanorods were formed. This thickening was observed in porous templates with diameters ~200-300 nm. For periods of time <1 hr, the ratio of wall thickness to outer diameter was ~0.11. As the length of time increased up to 12 hr, the ratio increased to ~0.14. Finally, for time periods ≥18 hr, nanorods formed. These results were consistent for molecular weights greater than or approximately equal to the entanglement molecular weight, $M_e$, ~19,100 g/mol [17]. For molecular weights below the $M_e$, only solid nanorods resulted. Figure 3 shows the correlation between the ratio of wall thickness to outer diameter and infiltration time of nanotubes formed with high molecular weight ($M_n > M_e$).
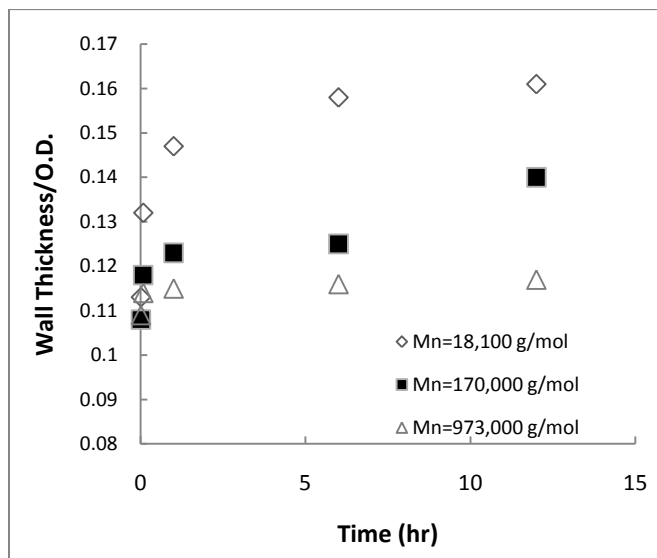


**Figure 10: Variation of nanopolymer wall thickness to outer diameter (O.D) with infiltration time during solution template wetting in commercial templates. ($M_e$~19,100 g/mol [17])**

The differences in the nanopolymer structures may arise from the variations in viscosity of each solution, and are therefore dependent on the molecular weight of the polymer. At the $M_e$, a rapid increase in viscosity occurs as a result of significant entanglements between polymer chains. Consequently, the filling of the template pores is slower than at molecular weights below the $M_e$, where entanglements are negligible. The increased filling time may yield hollow tube structures at $M_n > M_e$. When the initial solution enters the nanopore, phase separation results in the formation of a thin solid polymer layer on the surface. Due to the high solution viscosity, additional solution cannot flow down freely to compensate for any shrinkage or compositional variations. At $M_n < M_e$, phase separation may produce a thin surface layer as before. In this case, however, the polymer solution can flow rapidly and counteract any shrinkage. Thus, successive layers of phase separated polymer may form to eventually yield a solid nanorod.

The "layering" effect used to describe wall thickening in nanotubes is in agreement with work published by Schlitt et al [14]. They found that a linear relationship exists between the wall thickness and pore radius, where the thickness is ~50-60% of the pore radius [14]. Other authors have described the formation of polymer nanotubes to be dependent on the wetting behavior of the polymer solution [18]. Once the solution comes into contact with the template walls, a thin precursor film may form. Thickening of this film (or the nanotube walls) can occur as a result of the spreading of the low surface energy fluid. As viscosity is increased, the filling will occur in a "sink-like" flow, and is more difficult due to the opposition of the capillary pressure and the inertia and friction of the liquid [18]. These studies are both in agreement with our results, indicating that it is more difficult for the higher molecular weight polymer to completely fill the nano-channels, and that the gradual thickening of the tubular walls may occur through a layering mechanism.

**Effect of Pore Size**

The template pore size also plays a role in the ability to form hollow nanotubes during the template wetting method. Templates with various pore sizes were fabricated using the anodization procedure, and additionally commercial templates were used during experimentation. It was found that large pore sizes, ~200-300 nm enabled the formation of hollow structures. Smaller pores sizes, ~40-50 nm and ~60-70 nm did not generate nanotubes for any molecular weight. Rather, solid structures formed under all conditions, indicating the pore size has an effect on the ability of the polymer to fill and generate thin tubular walls. Figure 4 shows TEM images of typical structures formed in both small and large diameter nanoporous templates.
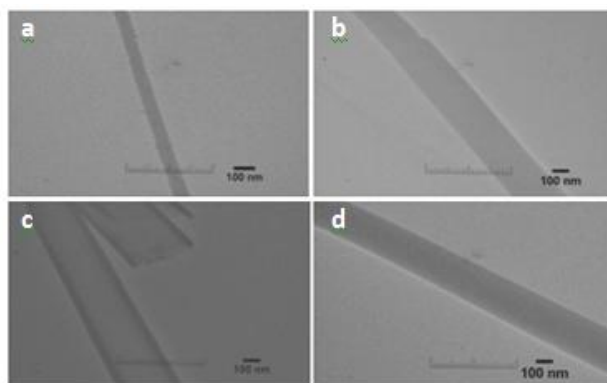


**Figure 11:** **TEM images of nanostructures formed during solution template wetting; a) 1 wt% PS ($M_n$=170,000 g/mol) infiltrated for 5 sec in homemade template; b) 1 wt% PS ($M_n$ =973,000 g/mol) infiltrated for 24 hr in commercial template; c) 1 wt% PS ($M_n$ =18,100 g/mol) infiltrated into commercial template for 1 hr; d) 1 wt% PS ($M_n$=10,000 g/mol) infiltrated for 5 min in commercial template**

These results are important for biomedical applications where nanotubes are being utilized for drug delivery. The hollow structures enable maximum drug loading, and the effect of pore size is thus critical to ensure the desired morphology can be achieved.

**Conclusion**

It was found that in addition to parameters such as polymer molecular weight, concentration, and infiltration technique, the effect of time and template pore size play a considerable role in the ability to form nanotubes during the solution template wetting method. For 1 wt% PS with $M_n > M_e$, hollow nanotubes formed for periods of infiltration time <18 hr. Thin tube walls formed initially by a layering mechanism, and after 18 hr, solid nanorods formed as the polymer walls converged. For PS with $M_n < M_e$, solid nanorods formed almost instantaneously. It was also found that the template pore size affected the final morphology of the polymer nanostructures. Small pore sizes of ~40-50 nm and ~60-70 nm produced solid nanorods while larger pores, ~200-300 nm, enabled tube formation. These effects of infiltration time and template pore size are therefore important parameters to consider during the solution wetting technique because they have a clear impact on the final morphology of the structures. For biomedical applications, understanding the role of these parameters is critical to maximize drug loading capacity as well as to predict the behavior of the nanostructures *in vivo*. Further development of a model to predict the morphology of the resulting structures is currently underway.

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Key Words: Template Assisted Nanofabrication, PS, nanotubes

# 3.4:  Publication in Process
# Role of Template Filling Techniques on Polymer Structure during the Production of Nanoparticles

Meghan Pasquali[1], Jianyu Liang[2], Satya Shivkumar[3]

*Worcester Polytechnic Institute*
*Materials Science & Engineering*
*100 Institute Rd, Worcester, Ma 01609*
*mpasqual@wpi.edu     jianyul@wpi.edu     shivkuma@wpi.edu*

## Keywords

Nanomaterials
Polymers

## Abstract

The solution template wetting method is a common technique used to fabricate elongated polymer nanostructures; however the parameters controlling the resulting morphology remain unclear.  Thus, this investigation aimed to identify and understand the physical mechanism of nanostructure formation during solution template wetting.  Experiments were performed with 1 wt% polystyrene solutions that were infiltrated into both commercial and homemade anodized aluminum oxide templates.  It was found that high molecular weight polymer solutions form hollow nanotubes for infiltration times <18 hr, while low molecular weight systems form solid nanorods.  Additionally, tube structures formed in commercial templates with 20-300nm pore sizes while rods formed in homemade templates with 40-50nm pore sizes.  Lastly, contact angle measurements were made with each polymer solution to confirm the wetting behavior of the various polymer solutions. These results were used to develop an understanding of the "layering" mechanism of nanostructure formation that occurs during solution template wetting.

## Introduction

Solution template wetting is a common method used to produce elongated, polymeric nanostructures because it is simple, cost effective, and generates highly uniform structures [1-6]. The technique utilizes a nanoporous template, typically made of anodized aluminum oxide (AAO), which is then infiltrated with a polymer solution. Once the polymer has hardened and the solvent has evaporated, the nano-polymer can be released through dissolution of the template [1]. The final morphology of the structures can range from small nanoparticles [4], to thin nanowires and fibers [7], to nanorods and hollow tubes [6,8]. Despite the successful fabrication of the architectures listed above, the definitive parameters that control the final morphology remain unclear. It is believed that the polymer molecular weight and concentration [8], solvent [4], and most recently the infiltration technique [9] may affect the resulting architecture.

Published research concerning the effect of polymer molecular weight on the morphology of structures (fabricated with the solution template wetting method) remains ambiguous. In general, most studies have been conducted with polystyrene (PS) due to the ease of fabrication and to the extensive data available about the rheological characteristics of the polymer. Schlitt *et al*. found that a high molecular weight PS ($M_n$>75,000 g/mol) is necessary for stable, tube structures to form, whereas solid nanorods form at low molecular weights [8]. Another research group reported that molecular weight does not have a significant effect on the morphology and that only solid nanorods can be formed with PS solutions [4]. Still other research has shown that the effect of entanglements (and thus molecular weight) may play a role in polymer stability, enabling thin tubular walls to form along the template pore walls [9]. The results concerning molecular weight are coupled with those pertaining to the necessary polymer concentration for hollow nanotube formation to occur. It has been indicated by some that 10 wt% polymer is required to form hollow nanotubes [8] while others have successfully reduced the polymer

concentration to 5 [10], 2.5 [6,11], 1 [9] and most recently as little as 0.5wt% [9,12].  These results are consistent for numerous polymers, including PS [8], polymethyl methacrylate (PMMA) [7], ethylene vinyl acetate (EVA) [10], and acrylonitrile-butadiene-styrene (ABS) [6].

The infiltration technique can be varied during solution wetting method, and may affect the resulting nanostructure morphology.  Most studies report a "single immersion" technique where the template is exposed to the polymer solution for a given amount of time, then extracted and allowed to dry while the solvent evaporates [4,8,11,12].  This period of immersion time may vary anywhere from less than an hour to several days [4,8,11,12].  An alternative method, a "multiple dipping" procedure, has recently been reported and highlights the effect of an intermediate evaporation step [9].  With this technique, the nanoporous template is subjected to multiple infiltrations by first being immersed in the polymer solution, extracted to dry, and then immersed again.  This procedure may be repeated for any number of immersion and extractions and can be used to produce polymer nanotubes at concentrations as little as 0.5wt%.  The outcomes from this study have motivated the present investigation to further explore the effect of the infiltration technique on the polymer morphology.  The results have been used to understand the mechanisms associated with nanostructure formation and the parameters governing tube to rod transition.

## Materials & Methods

Tetrahydrofuran (THF) ACS and PS with a range of number average molecular weights both above and below the entanglement molecular weight ($M_e$=19,100 g/mol [13] ($M_n$=4,000 g/mol and PD=1.00, $M_n$=10,000 g/mol and PD=1.06, $M_n$=170,000 g/mol and PD=2.06) were purchased from Sigma Aldrich.  PS  ($M_n$=18,100 g/mol and $M_n$=973,000 g/mol, PD=1.07) were purchased

from Scientific Polymer Sciences, New York, NY. Aluminum sheets used to fabricate AAO templates were purchased from ESPI Metals, Ashland, OR while commercial AAO *Anodisc* templates were purchased from Whatman.

Experiments were conducted with both commercial and homemade templates prepared in the laboratory. The details of the homemade template fabrication procedure have been previously reported [14], however are described in short below. First, aluminum sheets are electrochemically polished in a mixture of percloric acid and ethanol. The sheets are then anodized in 0.3M oxalic acid, at 40V and 10°C for a period of 16-24 hr. An unordered, porous layer of aluminum oxide forms on the surface of the aluminum (Figure 1a). This layer creates a hexagonal imprint on the aluminum sheet beneath which acts as a substrate to guide the nucleation and growth of an ordered array of nanopores (Figure 1b). The first layer of aluminum oxide is then removed in a mixture of chromic and phosphoric acid. Next, a second anodization is performed for 10-15 hr. A periodic and ordered layer of porous aluminum oxide forms on the surface, and eventually becomes the nanoporous template used during experimentation (Figure 1c). This top surface is separated from the underlying sheet of aluminum in a mercury chloride solution. Finally, the pores are widened in a solution of phosphoric acid (Figure 1d). A comparison of homemade and commercial templates is shown in Figure 2.

Polymer solutions of 1 wt% PS in THF were infiltrated into the AAO templates with a single immersion technique. The nanoporous templates were submerged in the polymer solutions for time periods ranging from 30s to 24hr. Following each timed immersion experiment, polymer filled templates were allowed to dry in ambient conditions, *i.e.* still air, 25°C, and 1atm for at least 24 hr. Then, the AAO templates were dissolved in 0.1M NaOH prior to characterization of

the PS structures with a JSM 7000F Scanning Electron Microscope (SEM) and JEOL 100CX Transmission Electron Microscope (TEM).

Water contact angle measurements were performed to determine the wetting behavior of polymer solutions on the AAO templates. Measurements were made with 1 wt% PS solutions in THF ($M_n$=4,000 g/mol, $M_n$=10,000 g/mol, $M_n$=18,100 g/mol, $M_n$=170,000 g/mol and $M_n$=973,000 g/mol) using two different techniques; 1) the Washburn method, 2) high speed video recording and analysis. The Washburn method was performed using a Ramé-Hart Contact Angle Goniometer, Model 100-22-100. Solvent droplets were ejected with a total volume of 5µl, and measurements made with DROPimage software. The second method used a Sony HDR-XR500V Hard Drive Camera to record 5µl solvent droplets deposited onto the AAO surface. Adobe Premiere Pro and ImageJ software programs were used to process the videos and measure the average contact angles.

## Results & Discussion

The formation of a nanostructure during the filling of the AAO template may depend on several factors including the capillary flow of the solution into the pore, infiltration at the walls, phase separation of the polymer and eventual buildup of a solid layer on the pore walls. The stability of this polymer layer may determine the final morphology. If a stable layer can form on the walls during infiltration, it can promote the formation of nanotubes. The growth of the polymer layer may also lead to eventual nanorod formation. Polymer concentration and molecular weight can have a major role in stabilizing the initial layer. For example, Tan *et al.* have varied the concentration of polymer from 2.5 to 10 wt% and found that defects result in nanotubes produced at 2.5%, uniform nanotubes form at 5%, and solid structures at 10% [6]. They

concluded that the polymer concentration affected the ability of the solution to coat the template pores, and at high concentrations there are many more macromolecules that enable thickening of the tube walls to continue until a solid structure results. Similarly, studies with PS have been conducted by Schlitt *et al.* where the concentration of polymer was varied between 3 and 10 wt% [8]. Song *et al.* have studied the effect of concentrations with PS (2.5, 5 and 10 wt%), and formed structures with varying wall thicknesses [11]. Again, it was determined by both groups that at low concentrations, the stability of the polymer was compromised, and collapsed or defect structures resulted while at high concentrations, stable structures were formed [8,11]. These studies indicate that the stabilization and growth of polymer films are dependent on the polymer concentration within the solution. However, other parameters in combination with the concentration can account for wall thickening and subsequent nanotube formation. Pasquali *et al.* have shown that even at concentrations as low as 1 and 0.5wt% PS, hollow nanotubes can be formed [9]. Note, however, that differences in the infiltration method may have enabled stabilization of the polymer layers at such low concentrations. Pasquali *et al.* used a multiple dipping technique that perhaps enabled solvent evaporation to occur between each infiltration while the previous studies used a single immersion technique. As a result of the multiple dipping, stabilization of the polymer may have occurred and allowed hollow nanotubes to form that have not previously been observed at such low polymer concentrations [9]. These conflicting arguments concerning the necessary concentration for stable polymer formation suggest that the infiltration method may have a significant impact on the final nanostructure morphology.

During the present investigation, the single immersion method was studied to determine if differences in the infiltration time impacted the final morphology, and as a result could explain

inconsistent results among various investigators. It is understood that during capillary flow, the polymer solution fills the template pores and phase separation occurs as a thin polymer layer is deposited on the pore walls [15]. Once the template is extracted from the polymer solution, solvent evaporation may promote stabilization of the polymer layer along the pore walls. The influence of infiltration time on the polymer structure and subsequent solvent evaporation that occur during the single immersion technique was studied in this investigation with 1 wt% PS-THF solutions. The dipping time, (single) was varied from 30s to 24hr and results showed that for a typical polymer molecular weight, ~170,000 g/mol, nanotube formation occurred below a critical infiltration time (~18hr). When the templates were infiltrated for $t \geq 18hr$, solid nanorods resulted. The diameters of all the nanostructures corresponded to the template pore diameters. Figure 3 shows the progression of tube to rod transition that occurred when the infiltration time was increased from relatively short to long infiltration times. The complete results from this study are summarized in Table 1. These results are consistent with Schlitt *et al.* who found that at similar high molecular weights, hollow tubes resulted when templates were infiltrated for 1 hr [8]. In addition, results showing that long infiltration times lead to solid structures are in agreement with Feng and Jin, who infiltrated templates for 24 hr and formed nanorods [4]. It is believed that if the initial polymer layer is able to stabilize along the pore walls, subsequent polymer build-up will occur until either 1) the template is extracted after relatively short infiltration times and hollow structures are formed, or 2) opposing polymer layers converge after long infiltration times to produce solid nanorods. This mechanism may differ for the multiple dipping method, during which the build-up of polymer layers is interrupted by the extraction of the template. As a result, solvent evaporation may occur between each dip and allow polymer

layers to stabilize. The consequential slow build-up of polymer layers may explain the resulting hollow nanotube architecture.

In addition to the infiltration method, the polymer molecular weight may also contribute to the resulting morphology of nanostructures formed during solution template wetting. Schlitt *et al.* reported that high molecular weight polymers are necessary to form hollow structures, while solid nanorods result at low molecular weights [8]. However, others have indicated that the interfacial polymer-template interactions have a greater impact than molecular weight, and are more significant in determining the resulting morphology [4]. During the present investigation, the polymer molecular weight was varied widely to determine the effects on the final nano-architecture. When the polymer molecular weight was $\geq$ 18,100 g/mol, hollow nanotubes resulted (for infiltration times < 18hr as previously described). When the molecular weight of the polymer was reduced to $M_n$ <18,100g/mol, solid nanorod architectures were produced (results are summarized in Table 1). A comparison of the morphologies is shown in Figure 4, and it can be noted that these results are in agreement with published research [8]. At high molecular weights, the build-up of stable polymer layers may occur slowly due to the high viscosity of the polymer solution. The resulting slow infiltration may prevent rapid polymer layer build-up and thus lead to eventual nanotube formation. Figure 5 illustrates the wall thickening that occurs over time during nanotube formation for solutions made with high molecular weight polymer. It can be seen that the rate of wall thickening is fastest (initially) at $M_n$=18,100g/mol, compared to the high molecular weight solutions with PS $M_n$=973,000 g/mol. As described previously, the rheological properties of the solutions may account for the varying rates of wall thickening. Additionally, the differences in viscosity may explain the relative wall thicknesses of nanostructures made from each of the solutions. Figure 6 indicates that the wall

thicknesses of nanostructures made from PS $M_n$=18,100 g/mol are greater than those from PS $M_n$=973,000 g/mol. The infiltration again may be slower for very high molecular weight polymer solutions, and thus fewer polymer layers may build-up. Figure 6 also highlights the relationship between the wall thickness and outer diameter of nanotubes formed with each solution. The graphs indicate that for all solutions, as the outer diameter of the nanotubes increases, the walls similarly become thicker. This behavior can be expected because an increased template pore diameter, and thus larger nanotube outer diameter, may enable greater fluid flow leading to increased polymer deposition along the pore walls. Schlitt *et al.* observed similar behavior where wall thicknesses of resulting nanotubes increased with pore radii, however the walls were thicker than those in this study [8]. They suggest that a de-wetting process may be occurring such that the wall thicknesses are more stable with increasing curvature of the capillary. Song *et al.* have also studied wall thicknesses of nanostructures made from 2.5 to 10 wt% PS and found that these thicknesses increased with polymer concentration from 50 to 80nm respectively, compared to results in the current study where thicknesses were ~25-50 nm for similarly high molecular weight polymer solutions [11]. These differences may be attributed to the polymer concentration. At 1 wt% concentrations, significantly fewer polymer chains may be deposited on the template pore walls than at 5 or 10 wt% concentrations typically used by others, and thus thinner polymer layers may form along the pore walls for a given time period. Finally, in contrast to the high molecular weight polymer solutions, low molecular weight polymer solutions resulted in solid structures. This may have occurred due to the significantly reduced viscosities that allow more rapid infiltration and subsequent build-up of polymer layers. These layers can grow from either end and likely converge to form the nanorod morphology.

The differences in rheological properties between high and low molecular weight polymer solutions can be further understood with respect to the entanglement molecular weight, $M_e$. This is the molecular weight at which the hydrodynamic volumes of polymer chains overlap. Above this molecular weight, the viscoelastic properties of a polymer are affected by entangled polymer chains [16]. For PS, this value is ~19,100 g/mol [13] and hence PS molecular weights used in this study were both above and below this value. In addition to $M_e$, the Berry number, $B_e$, can be used to describe the effect of entangled polymer chains and concentration, and is defined as [η]c, where η is the intrinsic viscosity and c is the polymer concentration [17]. When $B_e \geq 1$, the effects of entangled polymer chains contribute significantly to the rheological properties of the solution [17]. Furthermore, a critical concentration c* can be calculated that identifies the concentration at which the effects of polymer chain entanglements become important. The critical concentration can be approximated as c*~1/η [18]. These values, both c* and $B_e$ have been calculated for the various PS molecular weights used in this study. The c* decreases with increasing molecular weight from 22 wt% for PS with $M_n$=4,000 g/mol to 0.4 wt% for PS with $M_n$=973,000 g/mol. These critical concentrations show that low molecular weight polymer solutions require high concentrations for polymer molecules to interact and affect the rheological properties. Similarly, calculations of $B_e$ indicate that the effects of entangled polymer chains are not considerable unless high molecular weight polymer is used. Figure 7 shows that $B_e$=1 when PS $M_n$ ~350,000 g/mol. Thus there are significant differences in the rheological properties of the polymer solutions made from the low and high molecular weight polymer.

The wetting behavior of the polymer solutions must be considered in understanding the mechanism of nanostructure formation. It is believed that low molecular weight polymer solutions more easily infiltrate and wet the template pore walls than high molecular weight

polymer solutions. This anticipated behavior has been confirmed by contact angle measurements made on commercial AAO templates with 1 wt% PS-THF solutions (Table 2). Redon *et al.* demonstrated that the wetting of homemade AAO templates with solvents is correlated to both the polarity and surface tension properties of the fluid [19]. In this study, a relatively polar solvent (THF) was used, and the surface tension of the polymer solutions varied with the molecular weight of the polymer. Results confirm that a low molecular weight polymer solution (that therefore is not affected by molecular chain entanglements) more readily wets an AAO substrate than solutions made from high molecular weight polymer. A 1 wt% PS ($M_n$=4,000 g/mol) solution in THF results in a contact angle of 41.7°, however when the molecular weight of the polymer is increased to the entanglement molecular weight (approximately), the contact angle also increases to 50.0°. When the molecular weight of the polymer is even greater, $M_n$=973,000 g/mol, the contact angle increases to 56.6°. These results, summarized in Table 2, confirm the wetting behavior of the polymer solutions and may be used to describe the fluid flow through the nanopores. These results also suggest that there may be differences in the template surface properties between homemade and commercial templates. As previously mentioned, contact angles measured during the present investigation were made on commercial AAO templates while those reported in the literature were made on homemade templates. Redon *et al.* did not report measuring pure THF (the solvent used in this study), however results from their measurements with either toluene or hexane would be expected to be similar to pure THF due to comparable solubility properties. However, Redon *et al.* reported contact angles for toluene and hexane to be 68.9° and 64.5° respectively [19] while the contact angle of pure THF was measured to be 42.6° in the current study. These differences again may be attributed to the differences in surface properties of the two types of templates; homemade and commercial.

Another way to study nanostructure formation in nanochannels is to model the fluid flow with the Lucas Washburn (LW) equation. The equation relates the height of the liquid, H, to the permeation time t, capillary radius R, solution viscosity and surface tension η and γ respectively, and lastly the contact angle θ between the liquid and pore wall as:

$$H^2 = \frac{R\gamma \cos\theta}{2\eta} t$$

The templates used in the present investigation were 60µm thick and the pores had approximate capillary radii that ranged from ~100-150nm. Contact angle values and relative viscosities for the various polymer solutions substituted in this equation confirm that the templates are completely filled within milliseconds for low molecular weight polymer solutions, while high molecular weight solutions may fill the templates within 1 to 2 seconds. This fill time represents the initial infiltration of the low surface energy solutions into the high surface energy nanochannels. After this first infiltration occurs, a thin polymer layer coats the pore walls and has been reported by some to act as a "second-order" template [11]. The build-up of successive polymer layers may occur more slowly with each additional film due to the reduction in the overall surface energy of the substrate. For low molecular weight polymer solutions, the infiltration of polymer at the pore walls may still occur so rapidly that opposing polymer layers converge to form solid nanorods, while the infiltration of high molecular weight solutions is more difficult, and thus the build-up of layers is slower and results in hollow nanotubes.

Lastly, the template pore size may affect the infiltration of polymer into the nanopores, thus leading to differences in the final morphologies. Results showed that hollow nanotube structures formed in the large pore diameters of commercial templates (>200nm and for critical times), while independent of time, solid nanorods resulted in all homemade templates with small pore

diameters.  Representative TEM images are shown in Figure 8 and indicate that the diameters of resulting nanostructures corresponded well with the template pore sizes.   As previously indicated, the surface properties of the homemade and commercial templates may be different and thus may affect the structure formation.   Furthermore, there is a large area for solvent evaporation to occur in the pore diameters of commercial templates, and as a result may allow stabilization of polymer films to form nanotubes.  In contrast, the small pore sizes in homemade templates may promote early polymer layer convergence to form solid structures.

The culmination of this investigation has resulted in an understanding of the fundamental physical mechanism that controls nanostructure formation during the solution template wetting method.  Figure 9 shows a schematic of this physical mechanism.  The differences between the infiltration of low and high molecular weight polymer solutions are illustrated through a single pore and show the comparative capillary flow rates and polymer layer build-up.  It is known that when low surface energy polymer solutions infiltrate nanopores, spreading along the high surface energy pore walls occurs by capillary flow.  Polymer chains migrate outward during phase separation and are deposited on the pore walls.  This polymer-solvent separation further dilutes the solution, driving continuous filling and subsequent polymer-solvent separation.  The build-up of polymer layers or thickening of nanotube walls occurs as a result.  However, this progression continues more slowly with the addition of each polymer layer due to the reduction in surface energy of the pore wall.  When polymer with $M_n<M_e$ infiltrates the nanopores, spreading may occur easily and subsequent polymer film thickening may proceed rapidly (even with the reduced surface energy of the pore wall) due to the absence of polymer chain entanglements and low viscosity.  In contrast, high molecular weight polymer solutions in which the viscosity has been increased due to polymer chain entanglements may fill the nanopores

more slowly and lead to eventual nanotube formation after short infiltration times or rods after long infiltration times. With this fundamental understanding, researchers can better predict the final morphology of nanostructures formed during solution template wetting.

## Conclusions

The current investigation has demonstrated the physical mechanism of nanostructure formation during solution template wetting.  Specifically, the effects of infiltration technique, molecular weight, polymer chain entanglements, and template pore size were studied.  It was shown that the infiltration time affects the amount of polymer layer build-up that can occur, and thus short infiltration times typically result in nanotube formation while long infiltration times ($\geq$ 18hr) lead to nanorod formation.  Additionally, the molecular weight of the polymer may affect the nano-architecture.  High molecular weight polymer solutions ($M_n > M_e$) may infiltrate AAO templates more slowly than low molecular weight solutions ($M_n < M_e$), and yield hollow nanotubes.  In contrast, low molecular weight solutions produce solid nanostructures perhaps due to the reduced viscosity that enables rapid infiltration and polymer layer build-up.    Finally, the template pore size impacted the formation of hollow nanotubes; nanorods formed in small pores (40-50nm) while nanotubes formed in large pores (150-300nm).  From these experimental results, a fundamental "layering" mechanism of nanostructure formation is proposed and can be used to predict the morphology of nanostructures fabricated during solution template wetting.
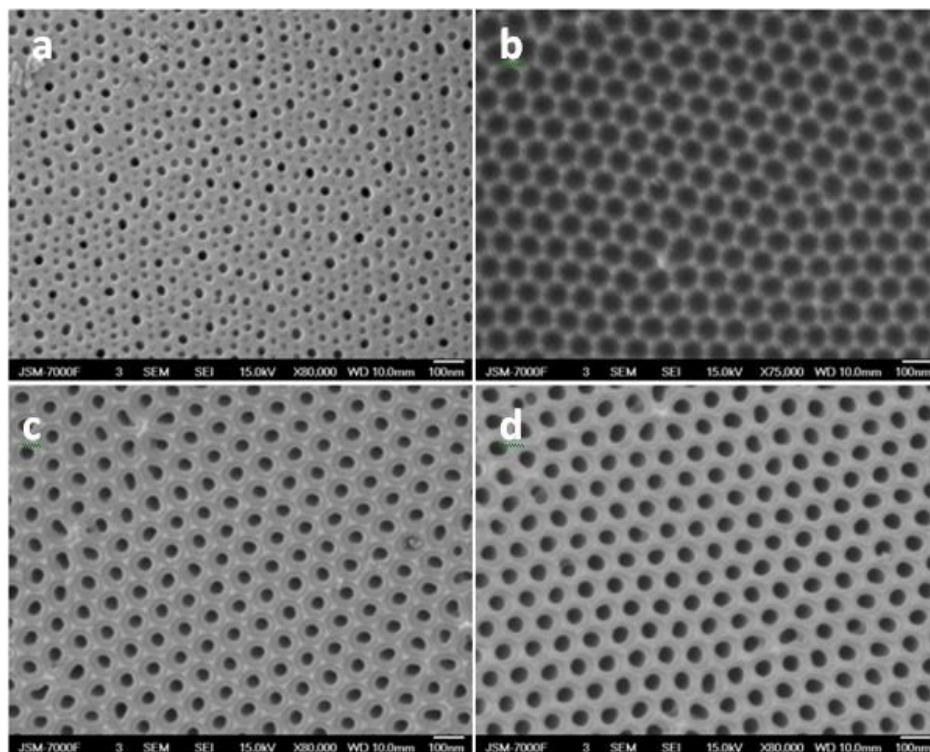
FIGURE 12: SEM IMAGES SHOWING THE RESULTS FOLLOWING EACH STEP OF THE ANODIZATION PROCEDURE DURING SYNTHESIS OF AAO TEMPLATES; (A) 1ST LAYER OF UNORDERED, POROUS ALUMINUM OXIDE, (B) HEXAGONAL IMPRINT ON THE ALUMINUM SHEET BENEATH FIRST LAYER OF ALUMINUM OXIDE, (C) 2ND LAYER OF ORDERED NANOPOROUS ALUMINUM OXIDE, (D) FINAL AAO TEMPLATE FOLLOWING SEPARATION FROM ALUMINUM AND PORE WIDENING STEEP
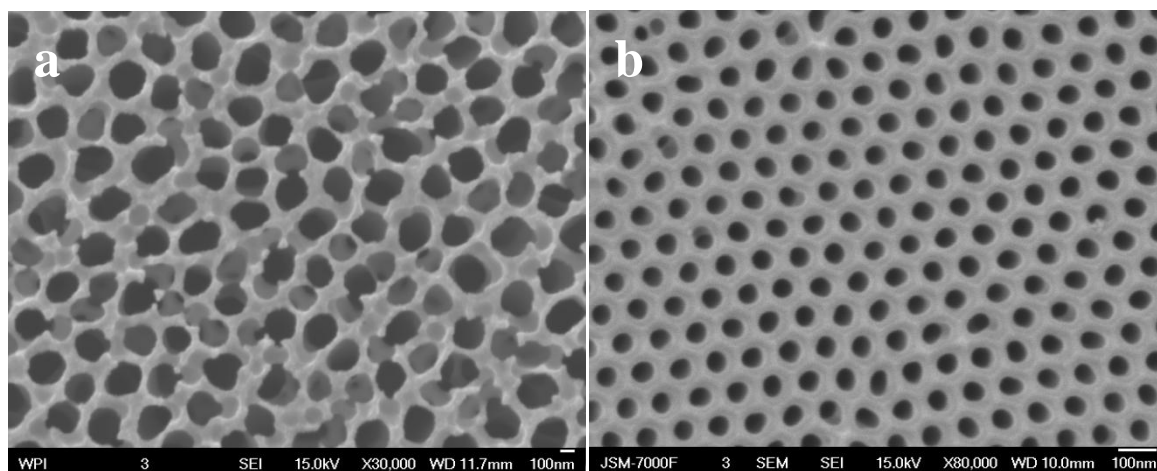
**FIGURE 13: COMPARISON OF COMMERCIAL (A) AND HOMEMADE (B) NANOPOROUS AAO TEMPLATES. COMMERCIAL TEMPLATES HAVE AN UNORDERED ARRAY OF PORES WITH DIAMETERS RANGING FROM 20-300NM WHILE HOMEMADE TEMPLATES HAVE A UNIFORM AND ORDERED DISTRIBUTION OF PORES 40-50NM IN SIZE.**
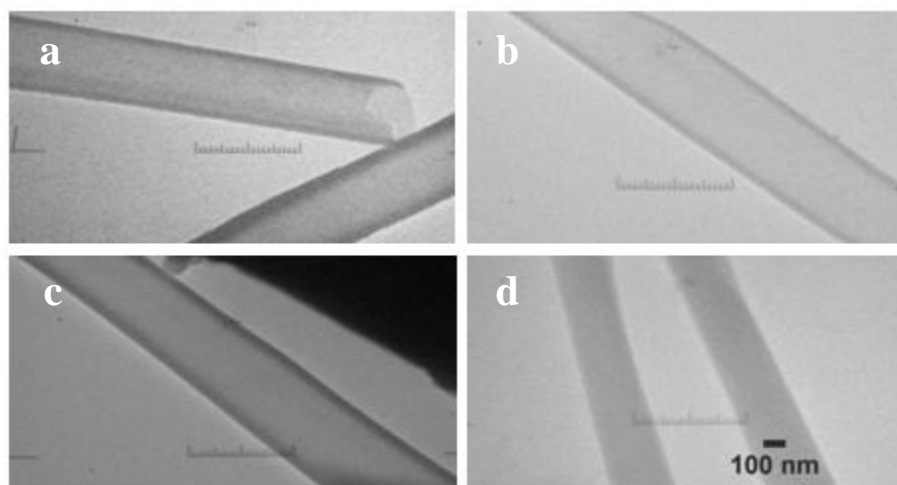


**FIGURE 14: TEM IMAGES OF NANOSTRUCTURES FORMED FROM 1 WT% PS ($M_N$=973,000 G/MOL) FOR VARYING TIMES IN COMMERCIAL TEMPLATES; (A) 5 MIN (TUBE); (B) 6 HR (TUBE); (C) 12 HR (TUBE); (D) 24 HR (ROD). THE TRANSITION FROM A TUBE TO ROD MORPHOLOGY OCCURS AT 18HR.**

**TABLE 2: SUMMARY OF POLYMER MORPHOLOGIES OBTAINED FROM A SINGLE INFILTRATION OF 1 WT% PS INTO COMMERCIAL TEMPLATES. HIGH MOLECULAR WEIGHT POLYMER SOLUTIONS INFILTRATED FOR T<18HR FORMED NANOTUBES. THE TRANSITION TO SOLID NANOROD FORMATION OCCURRED WHEN THE TIME WAS INCREASED TO ≥18HR. FOR LOW MOLECULAR WEIGHT POLYMER, NANORODS FORMED DURING ALL INFILTRATION TIMES.**

| PS $M_n$ (g/mol) | Single Infiltration Time | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 30 sec | 5 min | 30 min | 1 hr | 6 hr | 12 hr | 18 hr | 24 hr |
| 4,000 | ● | ● | ● | ● | ● | ● | ● | ● |
| 10,000 | ● | ● | ● | ● | ● | ● | ● | ● |
| 18,100 | ○ | ○ | ○ | ○ | ○ | ○ | ● | ● |
| 170,000 | ○ | ○ | ○ | ○ | ○ | ○ | ● | ● |
| 973,000 | ○ | ○ | ○ | ○ | ○ | ○ | ● | ● |

○ denotes hollow nanotube morphologies
● denotes solid nanorod morphologies
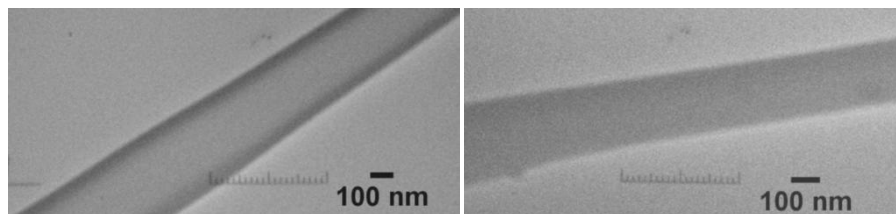


**FIGURE 15: TEM IMAGES COMPARING THE TUBE TO ROD TRANSITION THAT OCCURS WHEN THE MOLECULAR WEIGHT IS VARIED. LEFT, NANOTUBE FORMED AT MN=170,000 G/MOL VS RIGHT, NANOROD FORMED AT MN=10,000 G/MOL. (ALL OTHER PARAMETERS REMAINED CONSTANT)**
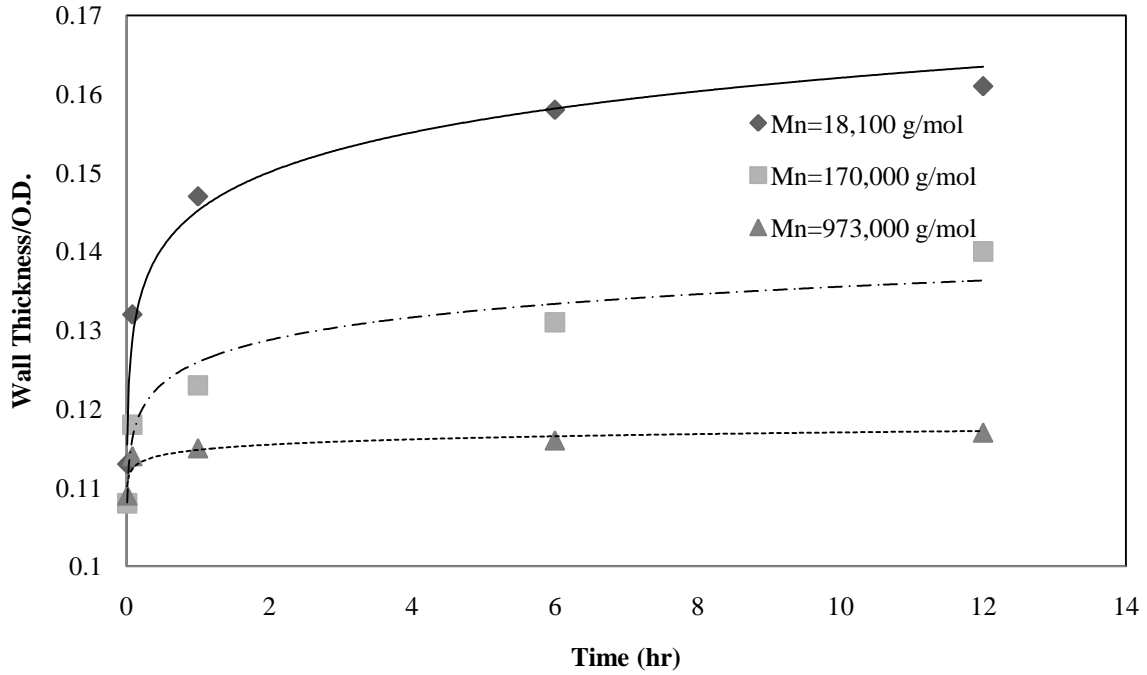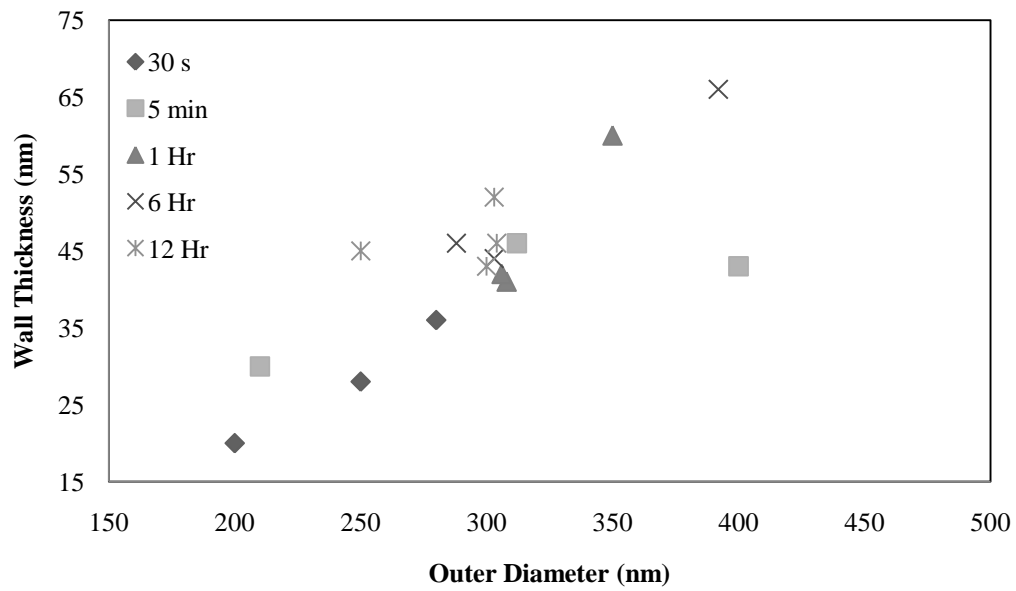
**FIGURE 16: VARIATION OF THE RATIO OF WALL THICKNESS/OUTER DIAMETER (O.D.) WITH TIME INDICATES THAT WALL THICKENING IS OCCURRING OVER TIME, AND ADDITIONALLY THAT THIS THICKENING IS MORE SIGNIFICANT NEAR THE ENTANGLEMENT MOLECULAR WEIGHT.**
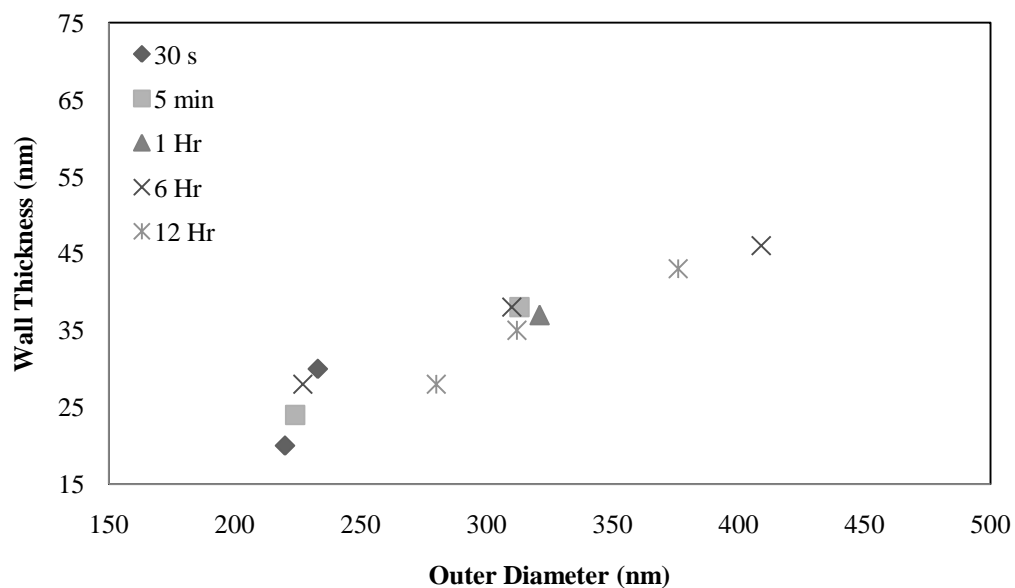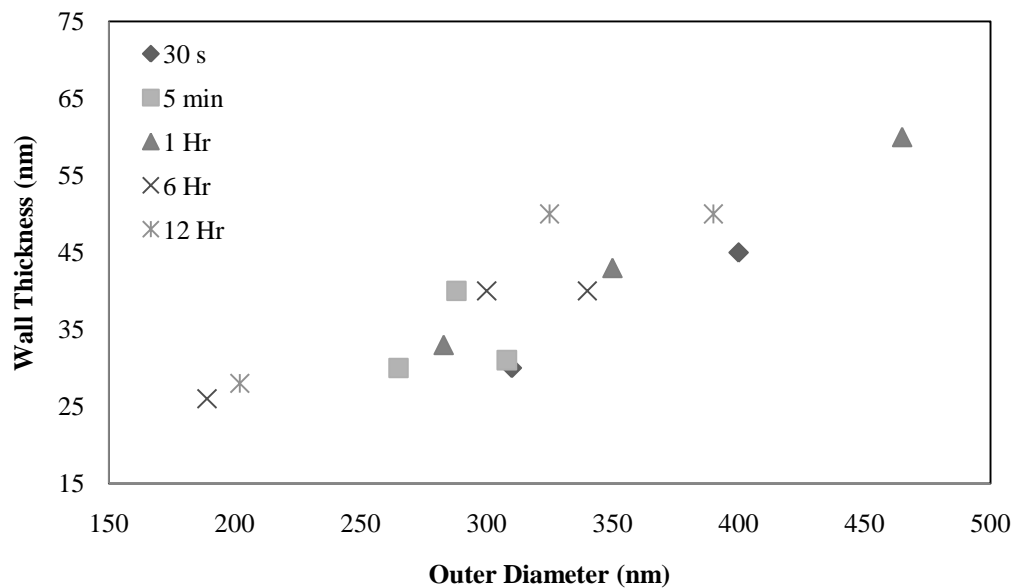
**FIGURE 17: VARIATION OF WALL THICKNESS WITH OUTER DIAMETER FOR HIGH MOLECULAR WEIGHT POLYMER SOLUTIONS. TOP:** $M_N$=18,100 G/MOL, **MIDDLE:** $M_N$ =170,000 G/MOL, **BOTTOM:** $M_N$ =973,000 G/MOL. **WALL THICKNESSES INCREASE THE MOST FOR** $M_N$ =18,100 G/MOL **LIKELY DUE TO THE DECREASED VISCOSITY OF THE SOLUTION COMPARED TO THE HIGHER MOLECULAR WEIGHT SOLUTIONS.**

**TABLE 3: CONTACT ANGLE MEASUREMENTS SHOW DECREASED WETTABILITY WITH INCREASING MOLECULAR WEIGHT.**

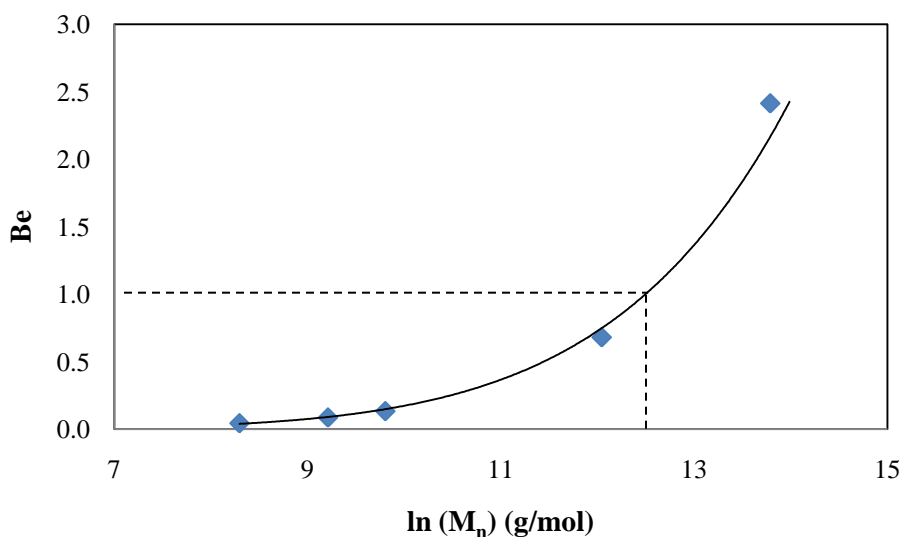| $M_n$ ( g/mol) | Contact Angle (°) |
|---|---|
| Pure THF | 42.6 |
| 4,000 | 41.7 |
| 10,000 | 43.0 |
| 18,100 | 50.0 |
| 170,000 | 53.9 |
| 973,000 | 56.6 |



**FIGURE 18: GRAPHICAL ILLUSTRATION OF THE VARIATION OF BE WITH POLYMER MOLECULAR WEIGHT. A BEST FIT CURVE INDICATES THAT $B_E$=1 AT $M_N$~ 350,000 G/MOL**
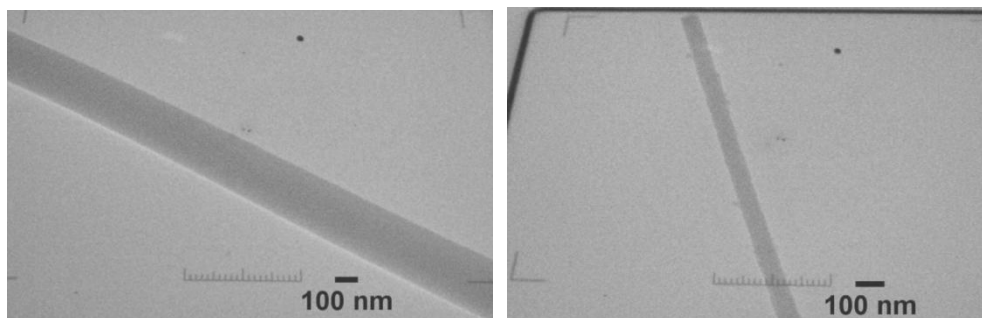


**FIGURE 19: TEM IMAGES SHOWING SOLID NANORODS FORMED IN COMMERCIAL (LEFT) AND HOMEMADE (RIGHT) AAO TEMPLATES. DIAMETERS CORRESPOND WELL WITH THE TEMPLATE PORE SIZES.**
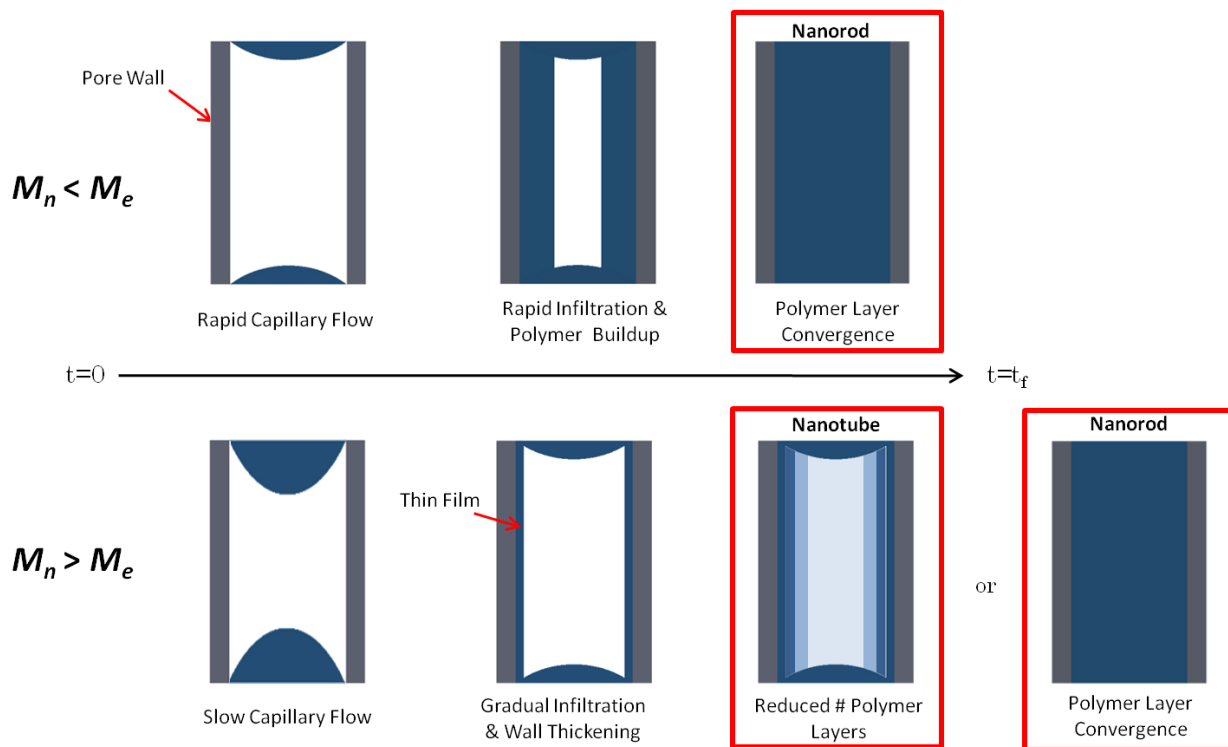
**FIGURE 20: SCHEMATIC OF LAYERING MECHANISM THAT OCCURS DURING SOLUTION TEMPLATE WETTING WITH LOW AND HIGH MOLECULAR WEIGHT POLYMER. LOW MOLECULAR WEIGHT POLYMER FILLS VERY RAPIDLY UNTIL THE ADDITION OF MANY POLYMER LAYERS CONVERGE TO FORM A SOLID STRUCTURE (TOP). HIGH MOLECULAR WEIGHT POLYMER FILLS MORE SLOWLY, AND POLYMER LAYERS STABILIZE ALONG THE PORE WALLS TO FORM NANOTUBES AFTER SHORT INFILTRATION TIMES OR RODS AFTER LONG INFILTRATION TIMES (BOTTOM).**

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# CHAPTER 4: CONCLUSIONS

This thesis comprises a collection of articles that highlight the governing parameters for nanotube and nanorod formation during solution template wetting. Through a series of experiments and analyses, these critical parameters have been identified and used to develop an understanding of the physical mechanism of nanostructure formation. This fundamental mechanism can thus be employed as a tool for medical researchers to predict the final morphology of structures fabricated with the solution template wetting method.

Initially, the ability to fabricate highly uniform, nanoporous AAO templates with a two-step anodization procedure was demonstrated. The resulting templates contained an ordered array of uniform pores with ~40-50nm diameters compared to commercially available templates, with non-uniform pore diameters ranging from ~20-300nm. Both template types were used throughout this investigation.

A "multiple dipping" technique was used to infiltrate the AAO templates and showed that stable nanotubes could be formed at polymer concentrations as low as 0.5 and 1 wt% (significantly lower than those previously reported). Reduced concentrations of 0.25 wt% resulted in collapsed or defect structures. It is believed that this multiple dipping technique may allow stabilization of a polymer film along the template pore walls, and likely occurs as a result of rapid solvent evaporation that takes place between each dipping of the template. During the more commonly used single immersion technique, this period of solvent evaporation may not occur until the pores are already completely filled with polymer, thus leading to solid nanorod formation.

The ability to reduce the polymer concentration and form nanotubes with the multiple dipping method lead to an investigation of nanostructure formation with the single immersion technique. The infiltration time was varied to determine if inconsistent results among published literature were due to differences in the infiltration technique. It was shown that nanotube formation is only possible below a critical infiltration time, and with polymer molecular weights above the entanglement molecular weight. Additionally, the effect of template pore size was investigated, and showed that nanotube formation is only possible in relatively large pore diameters (>150nm).

Finally, the culmination of this research was an understanding of the physical mechanism of nanostructure formation. The effects of the infiltration technique and time, polymer molecular weight, chain entanglements and pore size were demonstrated. It was shown that a "layering" mechanism leads to nanostructure formation during solution template wetting. The infiltration of a polymer solution must occur for $t < 18hr$ with high molecular weight polymer in order for stable polymer films to form along template pore walls and lead to nanotube formation. In contrast, low molecular weight polymer solutions exhibit significantly reduced rheological properties that may allow more rapid polymer film build up and thus lead to nanorod formation. Contact angle measurements confirmed the wetting behavior of both high and low molecular weight polymer solutions, and showed that low molecular weight polymer solutions more easily wet the AAO templates. All of these results validate the physical layering mechanism of nanostructure formation during solution template wetting.

The completion of this research investigation has resulted in an understanding of the mechanism of structure formation not previously known. The key parameters governing the tube to rod transition were identified and used to describe the "layering effect" of thin polymer films along

the template pore walls. This understanding is critical during the production of elongated nanostructures, and can be utilized during the further development of these structures for biomedical applications.