Block Copolymer Control Of Nanoscale Porous Materials

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BLOCK COPOLYMER CONTROL OF NANOSCALE POROUS MATERIALS

by

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Submitted in Partial Fulfillment of the Requirements
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DEDICATION

To My Mother
ACKNOWLEDGMENTS

This thesis is the results of works carried out in Stefik Research Group, at the University of South Carolina (USC) between September 2013 and March 2018 and with the kind help, support and companion I received from numerous people.

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ABSTRACT

The controlled fabrications of porous materials are crucial for a wide variety of uses spanning the gamut from energy applications to filtration. Despite decades of developments based upon block copolymer self-assembly there remain numerous limitations to achieve simple ends such as fully-tunable nanomaterials or well-defined macroscopic forms. For example, fundamental studies of nanostructure-performance relationships need systematic series of nanomaterials to identify the separate effects of wall and pore dimensions. Such precision control is impossible under the constraints of equilibrating systems. Persistent Micelle Templating (PMT) is rather based on kinetic control and enables robust and independent tuning of each feature. However, PMT development has been slow, requiring tedious polymerizations and extensive solution optimizations. These challenges were resolved with complete synthesis and templating within 24 hours combined with an efficient one-pot PMT titration approach supported by rapid SAXS modeling. Remarkable precision tuning was demonstrated with ~2 Å feature size increment. The PMT demonstrations to date were over a limited size range where these new developments enabled confirmation that tuning of solvent thermodynamics enables
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<td>ARGET</td>
<td>Activator regenerated electron transfer</td>
</tr>
<tr>
<td>ATRP</td>
<td>Atom transfer radical polymerization</td>
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<tr>
<td>DCC</td>
<td>Dicyclohexylcarodiimide</td>
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<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
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<tr>
<td>DMAP</td>
<td>4-Dimethylaminopyridine</td>
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<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<td>GISAXS</td>
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<td>GIWAXS</td>
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<tr>
<td>GPC</td>
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<td>H-PHA</td>
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<tr>
<td>HSQC</td>
<td>Heteronuclear single quantum coherence</td>
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<td>Micelle core templating</td>
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<td>NMR</td>
<td>Nuclear magnetic resonance</td>
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<tr>
<td>PEO-b-PHA</td>
<td>Poly(ethylene oxide-\textit{block}-hexyl acrylate)</td>
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<tr>
<td>PMT</td>
<td>Persistent micelle templates</td>
</tr>
<tr>
<td>PS-b-PLA</td>
<td>Poly(styrene-\textit{block}-lactide)</td>
</tr>
<tr>
<td>ROP</td>
<td>Ring opening polymerization</td>
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SAXS .................................................................................................................. Small angle X-ray scattering
SDA ....................................................................................................................... Structure directing agent
SEM ...................................................................................................................... Scanning electron microscopy
SIE ....................................................................................................................... Sonication induced exchange
TFA ...................................................................................................................... Trifluoroacetic acid
WAXS .................................................................................................................. Wide angle X-ray scattering
WMT ..................................................................................................................... Whole micelle templating
CHAPTER 1

OBJECTIVE AND INTRODUCTION
1.1 Research Objective

Controlled fabrication of block copolymer derived nanoscale porous materials is crucial to study in variety of fields, including the energy applications and ultrafiltration membranes. Block copolymers are defined as a class of macromolecules where two or more chemically dissimilar homopolymers are connected by a covalent bond. Being covalently bonded, the thermodynamically incompatible blocks can undergo microphase separation and results into various ordered nanoscale morphologies, termed as self-assembly.\textsuperscript{1-6} Block copolymer self-assembly in bulk and solution, both produces multiple complex morphologies, which have been studied extensively since last few decades. Despite decades of developments based upon block copolymer approaches there remain numerous limitations to achieve simple ends such as fully-tunable nanomaterials or well-defined macroscopic forms.

Tunable nanomaterials with independent control on architectural dimension is crucial to study the structure-property relationship in energy conversion and storage devices. Multiple transportation phenomena occur into various discrete locations while these porous nanostructured materials are employed into electrochemical studies. To understand each of the transportation processes better an independent architectural control is essential where one can have access on systematic alterations within a single morphology. Block copolymer equilibrium approach enables a large variety of ordered morphologies. However, the systematic control in architecture is limited under equilibrium. Equilibration is fundamentally incompatible with the concept of architectural tunability as any perturbation to a component triggers an associated change to the other component. This dissertation focuses on the addressing this question, how to get tunable
isomorphic architecture exploiting block copolymer self-assembly. Towards this end, creation of mesoporous materials with independent control on pore diameter and wall-dimension has been established under kinetic control, known as persistent micelle templating (PMT).

In other direction, mesoporous organic templates derived from block copolymer is also crucial for their applications in the size-selective separation. The self-assembly of block copolymers into ordered morphologies provides a scalable approach for the synthesis of ordered materials with uniform, nanoscale pores. Selective etching of a sacrificial block is the most widespread method of producing such porous polymers. Despite numerous etching chemistries for poly(styrene-\textit{b}-lactide) (PS-\textit{b}-PLA) type polymers reported in the literature, there remain challenges in balancing the extent of an etch process for PLA against the preservation of the nanostructure. The etching of thick polymer films is also challenging where high selectivity of the etchant is crucial to limit the degradation of the retained PS block while providing enough exposure time to etch through the PLA and across multiple grain boundaries. Therefore, an ideal etchant is needed which can quickly hydrolyze the PLA backbone while maintaining orthogonality towards PS. To this end, a trifluoroacetic acid (TFA) etching process is demonstrated with a higher etch rate of 14 nm/s while quantitatively preserving the starting morphology and without observable degradation of the remaining PS.

1.2 Dissertation Outline

This dissertation focuses on the controlled fabrication of nanoscale porous materials employing the (1) the concept of PMT and (2) the degradation of sacrificial PLA block. The preceding discussion highlights how to incorporate block copolymer self-
assembly approach into another level of precision fabrication of nanostructured materials. However, there are not yet simple self-assembly approach is to tailor each architectural dimension independently. Nanostructured materials with constant morphology symmetry are needed to study architecture-dependent properties so that the pathway tortuosity remains constant for each transport process. To this end, in this dissertation, I discussed few new strategies to improve the existing nanostructured materials fabrication employing kinetic control and manipulating thermodynamic parameters into the block copolymer system.

Chapter 2 demonstrates the development of a unique nanofabrication technique PMT that enables decoupled control over pore diameter and material wall-thickness via block copolymer self-assembly. The equilibration of block copolymer enables a wide variety of ordered morphologies where there are numerous systematic approaches for changing the morphology. However, this does not support the systematic alteration within a single morphology. PMT concept overcomes this issue by employing kinetically entrapped morphology and lowering the micelle exchange process significantly by increasing energy barrier. The earlier PMT works were mostly concentrated on the medium-to-large feature size control (25-60 nm pores and 11-57 nm wall dimension). Nonetheless, it is more challenging to regulate the smaller architecture under such kinetic control. Chapter 2 deals with the identification of PMT conditions for smaller feature sizes exploring (1) the synthesis of high $\chi$, amphiphilic block copolymer, poly(ethyleneoxide-block-hexylacrylate) in large scale without using any vacuum equipment and (2) introducing a solvent-cosolvent approach where $\chi$ could be manipulated by adding various amount of cosolvent. However, the solution guideline screening process is extensive and
time-consuming. Chapter 2 highlights a short and easy screening method to identify PMT condition. A combination of one-pot titration approach and small-angle X-ray scattering (SAXS) based geometric model were rationally designed to expedite PMT fabrication with constant ~13 nm pore size and tunable 6-9 nm wall-dimension.

Chapter 3 continues the development of PMT with smaller feature size where an improved method is reported to regulate PMT kinetics not by manipulating cosolvent amount anymore, rather by changing the major solvent to the one with higher solubility parameter. This approach shows better control of polymer kinetics via solution thermodynamics where the major solvent plays a role in maintaining the high energy barrier and a very small amount of cosolvent addition maintains the persistency. This method shows not only better control for tailoring the PMT window, it also avoids the possibility of formation of secondary pores into the material wall that causes by adding excess cosolvent. Moreover, a conceptual framework needed to realize PMT with <10 nm pores is in place by controlling polymer kinetics with solution thermodynamics.

The preceding discussions demonstrate the successful PMT control of wall-thickness tunability. Next, PMT is focused in tuning pore size. However, tunability is somewhat limited by the various ranges of molar masses that demands heavy synthetic effort. To overcome this challenge, a pore swelling approach under kinetic control is presented in chapter 4. It leads to the use of fewer polymers that needed to cover a wide range of length scales of both pore size and wall-thickness tunability from a single polymer. Preliminary results demonstrate continuously tunable pore size in the range of 15-25 nm from a single polymer using single sol-gel recipe. Additionally, wall-thickness tunability was performed successfully with the ~1.6-2x expanded pores. We believe this opens up the
possibility to improve PMT fabrication with varying range of pore sizes with minimal synthetic effort.

Next, chapter 5 turns the focus towards the mesoporous organic template fabrication from lactide containing block copolymer using a newly designed TFA etching method. This etching technique was developed for selective degradation of PLA from PS-\(b\)-PLA linear diblock copolymer and proves to be an ideal etchant for PLA where nanostructure is retained after 100% PLA removal, and no pore collapsing occurs. Additionally, the etching is quite fast and selective compared to the popular alkaline sodium hydroxide etching. The detailed synthesis, and self-assembly of PS-\(b\)-PLA along with the detail procedure of selective degradation of PLA is discussed in this chapter.

Finally, a summary including the results and possible future works is discussed in chapter 6. Collectively, this thesis discusses the improvements in porous templates fabrication employing block copolymer self-assembly that could equip to a higher level of precision fabrication.

1.3 References


CHAPTER 2

HOW TO MAKE PERSISTENT MICELLE TEMPLATES IN 24 HOURS AND KNOW IT USING X-RAY SCATTERING

2.1 Abstract

The controlled fabrication of nanoscale materials can enable new behaviors and properties as well as improved performance. For example, many electrochemical devices are made from porous materials where the architecture of both the porosity and the material each affect distinct processes. Recently, Persistent Micelle Templating (PMT) emerged as a unique nanofabrication technique that enables decoupled control over the porosity and wall material dimensions via self-assembly. PMT control relies upon kinetic entrapment to preserve the micelle diameter while adding material. However, the development of PMT is currently cumbersome where time-intensive polymerizations and solution parameter searches are both required. Here we report simple SAXS based geometric models that significantly expedite the identification of the PMT window with a one-pot titration-approach. The models also quantitatively predict the nominal template diameter and wall-thickness within the PMT window. This approach yielded the first PMT criteria for a low molar mass block copolymer with ~13 nm mesopores and continuously tunable wall-thickness with 2Å increment. Furthermore, we demonstrate an accelerated synthesis that includes custom polymer fabrication and micelle templating within 24 h. The polymer synthesis was demonstrated without high-vacuum equipment and only used low-cost, commercially available reagents. These advances will ease and accelerate the use of PMT for a wide gamut of nanomaterials investigations.

2.2 Introduction

Many nanostructured materials have been prepared by the self-assembly of micelle templates.\textsuperscript{1-9} A great diversity of template feature sizes have been achieved with the use of diverse block copolymer micelle dimensions, reflecting the wide-range of attainable molar
masses and solution conformations. The ability to generate nanostructured materials has resulted in numerous discoveries of remarkable behaviors, properties, and performance characteristics that are not otherwise present in analogous bulk materials. However, the discovery of new nano-enabled material is slowed by the difficulty in obtaining a wide range of architectural length scales. When deployed in electrochemical devices, the measurement of nanoscale porous materials fundamentally convolves multiple processes that occur in discrete locations, e.g. electrolyte transport through a pore or ion intercalation into a material wall. A better understanding of each of these processes requires a deconvolution approach with access to systematic nanostructure controls.

Recently persistent micelle templating (PMT) was invented to address this challenge. With PMT the formation of micelle templates is separated from the addition of material. This is achieved using kinetic entrapment of BCP micelles to prevent changes in template diameter from being coupled to changes in the material wall-thickness. The equilibrium micelle diameter is a balance of the enthalpy associated with the micelle-solution interface and the entropy associated with chain stretching, as well as other factors. Larger interfacial energy favors an increase in aggregation number and an increased micelle diameter that reduces the total surface area as balanced against the loss of configurational entropy from the induced chain stretching to fill space favors the reduction of micelle diameter. Micelles that are able to undergo exchange of polymer molecules between micelles thus undergo a change of micelle dimensions in response to changing solution conditions. Here the use of a high-χ block copolymers such as poly(ethylene oxide-block-hexyl acrylate) (PEO-b-PHA) facilitates the production of solution conditions that present a significant energetic barrier to reorganization. Thus changing the ratio of
material:template (M:T) allows one to independently control the resultant material wall-thickness while maintaining constant pore size and constant morphology symmetry. This is conceptually distinct from equilibrating approaches where changing solution conditions are coupled to multiple changes in the morphology.\textsuperscript{19-23} Current demonstrations of PMT control are limited to nominal pore dimensions between 24.9 and 57.0 nm and nominal material wall-thicknesses of 10.6 to 55.7 nm using 63-87 kg mol\textsuperscript{-1} BCPs.\textsuperscript{13,24} The extension of PMT to lower mass polymers with smaller associated feature sizes significantly expands current PMT capabilities. However, imposing a kinetic barrier on such small polymer chains is more challenging. The rate of single chain exchange is hypersensitive to chain length,\textsuperscript{25} and varies with chain architecture,\textsuperscript{26} and the energetic cost of solvophobe-solvent contacts embodied within the $\chi_{\text{solvophobe-solvent}}$ parameter.\textsuperscript{27} The identification a PMT window of conditions is guided by these thermodynamic principles, however the validation of PMT conditions requires custom polymers and tedious measurements on numerous samples. We present here SAXS based geometric models that significantly accelerate the identification of PMT conditions. These SAXS based models also enable the quantitative prediction of nominal template and material dimensions. Lastly, limited access to custom high-\(\chi\) block copolymers hampers the widespread adoption of PMT strategies. Towards this end we demonstrate a facile strategy to complete everything from polymer synthesis to micelle templating within 24 h. Lastly, a list of “tips and tricks”\textsuperscript{28} is provided to assist new researchers in establishing PMT control within their laboratories.
2.3 Experimental

Materials

Anhydrous, inhibitor free tetrahydrofuran (99%, Aldrich) and niobium (V) ethoxide (99.9%, Fisher) were stored inside a glovebox and used as received. Concentrated hydrochloric acid (37 wt%, ACS grade, VWR), poly(ethylene glycol) methyl ether (PEO-OH, $M_n$ 5000 g/mol, Aldrich), 2-bromopropionic acid (>99%, Aldrich), 4-(dimethylamino) pyridine (99%, Aldrich), $N,N'$-dicyclohexylcarbodiimide (99%, Aldrich), tris-(2-dimethylaminoethyl) amine (97%, Aldrich) and copper(I) bromide (99.99%, Aldrich) were used as received. Hexyl acrylate (96%, VWR) monomer was passed through basic alumina just prior to use. Anhydrous chloroform (>99%, Aldrich), hexane (>98.5%, Fisher), and dimethylformamide (DMF, 97%, Aldrich) were used as received.

PEO-$\beta$-PHA diblock copolymer synthesis

Step 1: Synthesis of poly(ethylene oxide)-Br (PEO-Br) macroinitiator

The PEO-Br macroinitiator was prepared by a simple esterification. The reaction was prepared by dissolving 20 g of 5 k $g\text{ mol}^{-1}$ PEO-OH in 100 mL of anhydrous chloroform. Then 0.72 mL of 2-bromopropionic acid was added dropwise to the polymer solution. The solution was set into an ice bath, followed by the addition of 400 mg of 4-dimethylaminopyridine and 1.65 g of dicyclohexylcarbodiimide using a molar ratio of PEO-OH:2-bromopropionic acid:4-dimethylaminopyridine:dicyclohexylcarbodiimide = 1:2:0.8:2. The reaction was stirred for 2 h at room temperature. Next, the solid was discarded which contained urea byproducts and the filtrate collected using Whatman V2 filter paper precipitated into 500 mL cold hexane. The crude product was next dissolved in
100 mL of chloroform and shaken with an equal volume of water. The aqueous layer was
discarded and the washing process by chloroform/water shaking and phase separation was
repeated a total of 3 times. The chloroform layer was precipitated into 300 mL of cold
hexane to isolate the PEO-Br macroinitiator. Photos of the procedure are provided in Figure
A1 with the time indicated. The resulting PEO-Br polymer was dried in the air with heating
to yield 78%. The PEO-Br was characterized by $^1$H NMR and GPC. The quantitative
esterification reaction of the hydroxyl group of poly(ethyleneglycol) methyl ether was
confirmed by comparing peak b to the peaks of a, c, d and e (Figure 2.1). $^1$H NMR (300
MHz, CDCl$_3$), δ (ppm): 4.39 (CHBrCOO), 4.31 (COOC$_2$H$_5$), 3.65 (CH$_2$CH$_2$O), 3.38
(CH$_3$O), 1.82 (CH$_3$).

**Step 2: Synthesis of PEO-b-PHA diblock copolymer**

The PEO-b-PHA was synthesized by atom transfer radical polymerization (ATRP)
using a reagent ratio of [hexyl acrylate]: [PEO-Br]:[Me$_6$TREN]:[Cu(I)]=150:1:0.5:0.5. To
a schlenk flask, 5 g PEO-Br macroinitiator (1 mmol) was added into 3 mL of DMF and the
mixture was stirred continuously at 40°C until a homogeneous solution was found. Next,
26.6 mL of inhibitor-free hexyl acrylate (150 mmol) was added into it and the flask was
sparged with nitrogen gas for 40 mins to remove dissolved oxygen. A catalyst stock
solution of 1 mL of toluene containing 71.7 mg Cu(I)Br (0.5 mmol), and 133.6 μL (0.5
mmol) Me$_6$TREN ligand was added to the reaction flask under flowing N$_2$ gas. This
reaction mixture was then placed into a pre-heated oil bath at 80 °C with constant stirring.
The polymerization was continued for 15 h. The reaction mixture was cooled before
exposing the solution to air. The crude polymerization solution was diluted with THF and
passed through a basic alumina column to remove copper salts. The product was
precipitated into 2-3-fold excess of cold methanol (-78 °C, using a dry ice bath). The collected polymer was dried on a hot plate at 40 °C 30 mins. Detailed photographs of the polymer synthesis are presented in Figure A.1 with the corresponding time indicated. The polymer was characterized by NMR and GPC. $^1$H NMR (300 MHz, CDCl$_3$), δ (ppm): 4.0 (COOCH$_2$), 2.27 (CHBrCOO), 1.90 (CH$_2$CHBrCOO).

![Figure 2.1](image)

Figure 2.1 $^1$H NMR spectra of commercial PEO-OH (a), the resulting PEO-Br macroinitiator (b), and the final PEO-$b$-PHA diblock copolymer (c). GPC traces of PEO-Br macroinitiator and PEO-$b$-PHA (d) confirm controlled chain growth. DLS measurements (e) of PEO-$b$-PHA micelles before and after sonication induced exchange.

**Persistent Micelle Templating of Nb$_2$O$_5$ thin films**

100 mg of dried PEO-$b$-PHA was dissolved in 10 mL of anhydrous, inhibitor free THF at room temperature followed by the dropwise addition of 880 µL of 37% w/w conc.
HCl with mild agitation. These quantities resulted in a solution with 7.5 wt% water used for most experiments, however the water ratio was sometimes varied as noted. The resulting micelle solution was sonicated for 5 min at room temperature using a Fisher Ultrasonic Bath (Cat No. FS28) to enhance equilibration under kinetically limited conditions. Next, the desired amount of niobium ethoxide was added to the polymer solution via a septum. The specific reagent quantities are detailed in Table 2.2. After each material addition, the solution was lightly agitated by rotating the vial to be upside down 5-6 times. Substrates were cleaned with piranha solution just prior to spin coating. Both coverslip glass (2 cm x 2 cm, 150 µm thick) and silicon wafers (2 cm x 2 cm) were used for transmission SAXS and GISAXS/SEM, respectively. The solutions were spin coated at 500 rpm for 1 min at 20-22°C using a home-made humidity-controlled spin coater (shown in Figure A.2). Instructions for how to build such a spin coater are available online. A constant 15% relative humidity was maintained throughout the entire coating process. The relative humidity was controlled by mixing dry air and wet that was produced by passing air through an aquarium stone submerged under DI water. The combined air streams were then passed through copper tube maintained at 40 °C to compensate for evaporative cooling. The relative humidity response to flow rates was measured with a certified digital hygrometer (Fisher Scientific Hygrometer) and verified with a mason hygrometer. A relative humidity calibration curve was established with a linear response to extrapolate low relative humidities below the hygrometer’s range of detection. After loading each substrate, the chamber was purged with humidity-controlled gas for 2 min. Immediately after spin coating, each sample was removed from the chamber and placed on a hot plate at 100 °C for 14 h to crosslink the material (“age”). After each coating, the
humidity chamber was wiped down and blown clean of solution residues with compressed air for 1 min. Please note that aging is important for morphology stability at ambient conditions. However, higher sample throughput is feasible by promptly measuring samples by SAXS. SEM samples were prepared similarly on silicon substrates and were subsequently calcined in air (Barnstead Thermolyne muffle furnace) at 5 °C min⁻¹ to 200 °C, then 15 °Cmin⁻¹ to 500 °C with 1 min hold, followed by natural cooling. Numerous measurements of pore size and wall thickness were measured on SEM images for statistically relevant descriptors. Photos of the experimental procedure are included in Figure A.2 with the time indicated.

**Characterization and analysis**

**Polymer Characterization**

All proton nuclear magnetic resonance (¹H NMR) spectra were recorded on Bruker Avance III HD 300. NMR samples were prepared in deuterated chloroform (CDCl₃) at a concentration of ~1 wt%. Molecular weight (Mₐ) and molar mass dispersity (Ɖ) were determined using a Waters gel permeation chromatography (GPC) instrument equipped with a 515 HPLC pump, a 2410 refractive index detector, and three styrage columns (HR1, HR3, and HR4 in the effective molecular weight range of 0.1-5, 0.5-30, and 5-600 kg mol⁻¹ respectively). THF was used as the eluent at 30°C at a flow rate of 1 mL min⁻¹. The GPC was calibrated with PS standards (2,570, 1,090, 579, 246, 130, 67.5, 34.8, 18.1, 10.4, 3.4, 1.6 kg mol⁻¹) obtained from Polymer Laboratories. GPC samples were prepared by dissolving the sample in THF at a concentration of 2.0 mgmL⁻¹ and were filtered (0.2 μm) just prior to injection. Dynamic light scattering (DLS) measurements of micelle
hydrodynamic diameter were measured using a Zetasizer Nanoseries ZEN3690 instrument. The polymer solutions for DLS were filtered (0.2 µm) just prior to measurement at room temperature. A viscosity of 0.455 cP and refractive index of 1.41 were used for DLS analysis.

**X-Ray Measurements**

X-ray experiments were conducted using a SAXSLab Ganesha at the South Carolina SAXS Collaborative. A Xenocs GeniX3D microfocus source was used with a Cu target to generate a monochromic beam with a 0.154 nm wavelength. The instrument was calibrated using National Institute of Standards and Technology (NIST) reference material 640c silicon powder with the peak position at $2\theta=28.44^\circ$ where $2\theta$ is the total scattering angle. A Pilatus 300 K detector (Dectris) was used to collect the two-dimensional (2D) scattering patterns.

All small-angle X-ray Scattering (SAXS) data were acquired with an X-ray flux of ~4.1 M photons/s incident upon the sample and a sample-to-detector distance of 1040 mm. GISAXS samples were tilted to have an incident angle ($\alpha_i$) of 0.24°. Transmission SAXS was measured normal to sample substrates to observe the purely in-plane morphology. These 2D images were azimuthally integrated to yield the scattering vector and intensity. Each scattering curve was background subtracted to remove the minor substrate contribution. Peak positions were fitted with Gaussian functions using custom Matlab software. Wide-angle X-ray scattering were acquired with an incident angle ($\alpha_i$) of 8° and a 104.5 mm sample-to-detector distance.
Scanning Electron Microscopy (SEM)

The top-view images of calcined films were acquired with a Zeiss Ultraplus thermal field emission SEM using an acceleration voltage of 5 keV and an in-lens secondary electron detector. The working distance was maintained at ~3 mm. Hundreds of measurements were made on each sample condition to yield statistically significant metrics of pore diameter, wall-thickness, and $d_{\text{micelle-to-micelle}}$.

Characterization of PEO Crystallinity

Bulk samples were prepared by casting sample solutions in a teflon dish at 60°C. The resulting powder was characterized using a TA Q2000 differential scanning calorimetry (DSC) instrument under nitrogen ($N_2$ flow rate 25 L min$^{-1}$). Approximately 28.7 mg of the powder sample was heated from room temperature to 160 °C, held at this temperature for 2 min to remove thermal history and cooled to -10 °C and further heated to 160 °C at a rate of 10 °C min$^{-1}$. The data was collected from second heating scan. The bulk sample was also measured by WAXS.

Geometric Based SAXS Model

The micelle core templating (MCT) and whole micelle templating (WMT) geometric SAXS models are derived in the Appendix A. The trend in d-spacing expansion was used to easily identify the exit from PMT conditions. The geometric models were fitted to the calculated d-spacing series within the apparent PMT window using a least squares optimization for 2 fit parameters ($\beta$ and $\gamma$). The modeling of wall-thickness utilized an additional fit term ($\alpha$) that was also determined by least squares optimization. SAXS based geometric models were used to 1) predict PMT titration curves for expected trends in d-
spacing, template diameter, and wall-thickness with changing M:T and 2) to estimate template diameter and wall-thickness based upon measured SAXS data.

2.4 Results and Discussion

Easy synthesis of PEO-\textit{b}-PHA in 20 h 30 min

Facile access to specialty block copolymers will expand the use of PMT. PMT relies upon kinetically trapped micelles that are used to template materials. Thus far, PMT has required the use of custom fabricated block copolymers to achieve the high-\(\chi_N\) solution conditions that are needed to inhibit the exchange of polymer chains between micelles.\(^{13}\) For example, widely produced BCP such as Pluronics imply a low-\(\chi_N\) barrier that is likely unsuitable for PMT. Likewise, commercially available BCP with high-\(\chi_N\) are prohibitively expensive, sometimes >\(\$100\) per g. Many custom BCP have been synthesized for nanomaterial fabrication,\(^{31-38}\) however these often rely on specialty equipment found in dedicated synthetic labs. Controlled radical polymerizations are very tolerant to impurities and may be thoughtfully enabled in capital-constrained environments with e.g. ATRP.\(^{39}\) An ATRP macroinitiator was synthesized from monochelic PEO-OH using a simple Steglich esterification to form PEO-Br.\(^{29,40}\) \(^1\)H NMR confirmed quantitative chain-end conversion (Figure 2.1 a,b). The PEO-Br macroinitiator was then chain extended by conventional ATRP to yield PEO-\textit{b}-PHA as confirmed by \(^1\)H NMR and GPC (Figure 2.1 c,d). Please note that for the sake of demonstration, the polymer presented here did not require use of vacuum equipment: oxygen was removed from the polymerization solution by sparging with \(N_2\) and the polymer was recovered by drying on a hot plate. Also, simple solution-based purification techniques were used to remove contaminants based on column adsorption, precipitation, and extraction at particular steps. This approach allowed the
preparation of 12.7 k g mol\(^{-1}\) PEO-\(b\)-PHA with 38 vol\% PEO and with narrow molar mass dispersity of 1.10 using only common laboratory glassware (Table 2.1). The total polymer synthesis was complete in 20.5 h from start-to-finish (Figure A.1). The cost of PEO-\(b\)-PHA is not prohibitive and was crudely estimated as \(~\$0.50\) g\(^{-1}\) based on $0.35 g^{-1}$ for hexyl acrylate and $0.22 g^{-1}$ for PEO-OH. The resulting 5 g of PEO-\(b\)-PHA were sufficient to prepare 50 solutions, each producing 40 films, for a total of 2,000 possible samples.

Table 2.1 PEO-\(b\)-PHA Characterization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(M_n,\text{PEO}) (g/mol)</th>
<th>(M_n,\text{PHA}) (g/mol)</th>
<th>Total (M_n) (g/mol)</th>
<th>(D)</th>
<th>(f_{\text{PEO}})</th>
<th>(f_{\text{PHA}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-(b)-PHA</td>
<td>5,000</td>
<td>7,700</td>
<td>12,700</td>
<td>1.10</td>
<td>0.38</td>
<td>0.62</td>
</tr>
</tbody>
</table>

\(a\) obtained from \(^1\)H NMR analysis, \(b\) obtained from GPC analysis, \(c\) volume fractions (\(f^v\)) calculated using densities\(^{13,40}\): PHA = 1.065 g cm\(^{-3}\), PEO = 1.064 g cm\(^{-3}\).

Micellization of PEO-\(b\)-PHA

The formation of micelles is the quintessential first step of PMT. PEO-\(b\)-PHA was dissolved in THF, a solvent that is relatively non-selective and does not result in detectable micellization of PEO-\(b\)-PHA.\(^{24}\) Aqueous HCl was then added dropwise to form micelles under kinetically challenging high-\(\chi_N\) solution conditions. These micelles were then sonicated for 5 min to promote sonication induced exchange (SIE)\(^{24}\) for the production of well-defined micelles with reduced dispersity (Figure 2.1e, Table A.1). The micelle hydrodynamic radius shifted from 33.5 to 21.4 nm with a corresponding reduction of standard deviation from 7.3 to 3.1 nm after 5 min sonication. SIE was recently discovered and likely operates on a similar surface-limited mechanism as agitation-induced chain
exchange.\textsuperscript{41-42} Well-defined PEO-	extit{b}-PHA persistent micelles were then used to template materials under kinetically challenging high-\(\chi_N\) solution conditions, \textit{vide infra}.

**Material Templating with PEO-	extit{b}-PHA Micelles**

Series of mesoporous samples were prepared by templating a material with PEO-	extit{b}-PHA micelles. Here we first elaborate the morphology characteristics of a particular sample before discussing trends within sample series. The mesoporous sample W7.5-1.21 was prepared using a THF/HCl solution with an initial composition of 7.5 wt\% water and M:T=1.21. In this case the material is Nb\(_2\)O\(_5\) and the template is PEO-	extit{b}-PHA micelles. Our geometric model described below relies on a simple conservation of volume combined with a correlation of scattering measurements to the nominal micelle-to-micelle spacing (Scheme 2.1). The \(>500\) nm thick films (Figure A.3) measured here provided sufficient SAXS signal with a transmission configuration with 5-120 min exposures (Figure 2.2b). For much thinner films, GISAXS would provide a viable path to mitigate the reduced sample scattering volume.\textsuperscript{43-47} The GISAXS geometry can enhance the SAXS signal and can also be used to probe depth-dependent features as a function of incident angle.\textsuperscript{43,44,46,48-49} Sample W7.5-1.21 exhibited a textured GISAXS pattern (Figure 2.2a) similar to prior reports\textsuperscript{50} of a mixed [100] and [110] textured body centered cubic (BCC) morphology with polydispersity of sphere diameter. Cross-sectional SEM measurements did not identify any morphology trends along the vertical direction (Figure A.3). Similarly, the transmission SAXS profiles exhibited several localized rings of intensity. The 2D transmission SAXS images where quite isotropic and symmetric, consisting of purely in-plane information. Azimuthal integration yielded two clearly defined peaks with an approximate ratio of 1:1.8 (Figure 2.2b). The scattering pattern could be indexed similar to prior reports of a
polydisperse BCC morphology.\textsuperscript{50} The combined interpretation of GISAXS and SAXS data of W7.5-1.21 were rather equivocal, despite the ability to index the observed maxima of scattering intensity, e.g. BCC \((q_{hkl}/q_{100})^2 = 2, 4, 6, 8\). For example, the disordered packing of spheres\textsuperscript{51} results in similar scattering profiles, however the SEM data exhibits clear short range ordering, consistent with a paracrystal. The first SAXS maximum closely matches the micelle-to-micelle spacing determined by SEM, which is not consistent with a BCC space group. The combination of SAXS and SEM are thus most consistent with a paracrystalline system that has limited long-range order and significant short-range order. The ambiguity of structure factor interpretation, however, is resolved by using a symmetry independent approach that correlates SAXS peaks to the micelle-to-micelle spacing with a scalar \(S\), \textit{vide infra}. Real-space images of calcined samples were acquired by SEM where mesopores (dark) were observed within niobium oxide walls (light). More than one hundred measurements were taken to quantify the average template diameter and wall-thickness as well as the corresponding standard deviations and standard errors of the mean (Table 2.3). The in-plane morphology of the top-surface contained regions consistent with 2-fold symmetry of [110] and 4-fold symmetry of [100] textured cubic grains, but also contained dispersity and disorder (Figure 2.2c). For example, comparing the average pore diameter of 13.15 nm and the standard deviation of 2.75 nm indicates a moderate degree of variation that would reasonably hamper sphere packing for long-range order. We note that size distributions can alternatively be measured with SAXS and GISAXS form factor fitting\textsuperscript{52-54} after accounting for the instrumental broadening factor. SAXS measurements before and after calcination confirmed that the nanostructure in-plane periodicity did not change upon calcination (Figure A.4), despite the typical out-of-plane contraction
associated with densification. The GIWAXS of Nb$_2$O$_5$ film after calcination to 500 °C demonstrated crystalline material (Figure A.5). Nanostructured porous materials were prepared with well-defined dimensions for template pores and material walls.

Scheme 2.1 SAXS based geometry models were used to deconvolve the template diameter and wall-thickness from the characteristic periodicity measured by SAXS. A whole micelle template, WMT (a) and micelle core template, MCT (b) model were considered.

Figure 2.2 PMT was used to generate mesoporous Nb$_2$O$_5$ materials. The morphology of sample W7.5-1.21 was characterized by 2D GISAXS (a) and transmission SAXS (b).
Porous films were observed by SEM (c) after calcination of sample W7.5-1.21. The color scale in (a) corresponds to the log of X-ray intensity. Here, \( q = \frac{4\pi \sin(\theta)}{\lambda} \) where \( q \) is the scattering vector, \( 2\theta \) is the total scattering angle, and \( \lambda \) is the wavelength.

**Titration of Continuously Variable Nanostructures**

The production of continuously tunable nanomaterials broadly enables new systematic investigations within the nanomaterials community. This addresses the broad challenge of using limited sample variations to establish correlations of nanoscale architectures to their resulting changes in behavior, properties, and performance. The use of PMT conditions enables the production of continuously tunable nanomaterials via titration. So long as the solution conditions maintain persistent micelle dimensions, the additional material directly increases the material wall-thickness without changing the nominal pore size resulting from the template. PMT enables this tunability while maintaining constant morphology symmetry, allowing the resulting behaviors to be studied without changes to sample tortuosity.

The continuous titration of tunable nanostructures was demonstrated with a one-pot approach. Here a persistent micelle solution was prepared and homogenized by SIE. Please note that at ambient conditions, in the absence of SIE, the micelle dimensions remain constant due to kinetic entrapment. Material precursors were added to the persistent micelle solutions via a septum, and an aliquot of the resulting mixture was then applied to substrates by spin coating. Here the target material was \( \text{Nb}_2\text{O}_5 \) added via an alkoxide precursor. Libraries of micelle templated materials were produced through repetition of material precursor additions followed by coating after each step. A simple mass calculation allows one to track the changing solution composition as a function of each addition and aliquot removal. Table 2.2 shows one such series with 12 steps of material additions to a
micelle solution starting with 7.5wt% water. The trends in architecture changes were tracked by a combination of SAXS and SEM. The SAXS patterns continuously shifted the first peak position to lower q with material additions (Figure 2.3a), consistent with a lattice expansion in real space (Figure 2.3b). Sample W7.5-2.07 deviated from this overall trend and was the first sample in the series where the nominal SEM pore size changed, indicating departure from the PMT window. This observation was consistent with two separate experimental trials under the same conditions and shows the excellent reproducibility of kinetic entrapment (Figure 2.3b). W7.5 samples with M:T ≥ 2.42 exhibited a broadening of the SAXS profile where samples with M:T ≥ 2.66 exhibited a bimodal first peak, suggesting a morphology change. SEM measurements of samples W7.5-1.13 through W7.5-1.94 identified a constant nominal pore dimension of 12.74 nm, with minor variation (Figure 2.4, Table 2.3). In contrast, samples W7.5-2.07 through W7.5-2.47 exhibited reduced nominal pore sizes between 9.49 and 10.38 nm. This reduced nominal pore size is consistent with a departure from the PMT condition window. This is expected since material addition via a metal alkoxide results in hydrolysis that consumes water and reduces the energetic barrier χ_{PHA-solution} to single chain exchange.\textsuperscript{13,27} Thus, the window for PMT conditions with series W7.5 was identified for M:T < 2.00, after which the reduced kinetic barrier allows a decreased micelle diameter on the experimental timescale (Figure 2.3c). For the same W7.5 series, the Nb\textsubscript{2}O\textsubscript{5} wall-thickness was observed by SEM to monotonically increase from 6.74 to 9.30 nm within the PMT window (Figure 2.3d, Table 2.3). A PMT titration was shown to enable sample series with continuously tunable material wall-thickness and constant templated pore dimensions.
Table 2.2 Titration of sample series W7.5, with 7.5wt% water in the starting micelle solution.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Nb(OEt)\textsubscript{5} added (mL)</th>
<th>Aliquot mass removed (g)</th>
<th>Water:Nb ratio</th>
<th>M:T ratio \textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>W7.5-1.13</td>
<td>0.206</td>
<td>0.566</td>
<td>41.41</td>
<td>1.13</td>
</tr>
<tr>
<td>W7.5-1.21</td>
<td>0.220</td>
<td>0.623</td>
<td>36.14</td>
<td>1.21</td>
</tr>
<tr>
<td>W7.5-1.46</td>
<td>0.265</td>
<td>0.365</td>
<td>26.15</td>
<td>1.46</td>
</tr>
<tr>
<td>W7.5-1.58</td>
<td>0.288</td>
<td>0.349</td>
<td>22.88</td>
<td>1.58</td>
</tr>
<tr>
<td>W7.5-1.77</td>
<td>0.323</td>
<td>0.441</td>
<td>19.37</td>
<td>1.77</td>
</tr>
<tr>
<td>W7.5-1.94</td>
<td>0.354</td>
<td>0.715</td>
<td>16.51</td>
<td>1.94</td>
</tr>
<tr>
<td>W7.5-2.07</td>
<td>0.376</td>
<td>0.360</td>
<td>13.75</td>
<td>2.07</td>
</tr>
<tr>
<td>W7.5-2.24</td>
<td>0.407</td>
<td>0.453</td>
<td>11.89</td>
<td>2.24</td>
</tr>
<tr>
<td>W7.5-2.30</td>
<td>0.419</td>
<td>0.417</td>
<td>10.56</td>
<td>2.30</td>
</tr>
<tr>
<td>W7.5-2.42</td>
<td>0.441</td>
<td>0.559</td>
<td>9.19</td>
<td>2.42</td>
</tr>
<tr>
<td>W7.5-2.47</td>
<td>0.449</td>
<td>0.421</td>
<td>7.91</td>
<td>2.47</td>
</tr>
<tr>
<td>W7.5-2.66</td>
<td>0.483</td>
<td>0.484</td>
<td>6.60</td>
<td>2.66</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The starting micelle solution was prepared by dissolving 100 mg polymer in 10 mL THF followed by the dropwise addition of 880 \textmu L of HCl. \textsuperscript{b}M:T ratio is the Nb\textsubscript{2}O\textsubscript{5}-to-polymer mass ratio in the final material assuming complete conversion of oxide precursor.

Figure 2.3 SAXS of sample series W7.5 with increasing material:template ratio (a, Trial 1). The shifting first-peak position corresponds to an increasing d-spacing (2\pi/q) (b). The scattering data in (a) were offset vertically for clarity. The increasing d-spacing was correlated to an expanding micelle-to-micelle spacing with a MCT geometric model (b, dotted line). Data fitting allowed the micelle-to-micelle spacing to be deconvolved into the...
micelle diameter (c) and material wall-thickness (d). Here the average pore diameters calculated from SEM measurements were used as a proxy for the nominal template diameters. A combined density term was fitted, allowing the prediction of a PMT titration curve as well as the extraction of pore diameter (a) and wall-thickness (b) dimensions from SAXS data. The MCT model was used based on fit parameters identified in Table 2.5. Model limitations for higher M:T ratios are discussed in the text. Changes in template diameter (c) identify the transition from persistent micelles to dynamic micelles (vertical dash-dot line).

Figure 2.4 SEM images of sample series W7.5 after calcination, in order of increasing material:template ratio, W7.5-1.13 (a) W7.5-1.21 (b) W7.5-1.39 (c) W7.5-1.46 (d) W7.5-1.58 (e) W7.5-1.77 (f) W7.5-1.94 (g) W7.5-2.07 (h) W7.5-2.24 (i) W7.5-2.30 (j) W7.5-2.42 (k) and W7.5-2.47 (l).

**Use of a SAXS based Geometric Model to Identify Architectural Parameters and PMT Conditions**

We derived simple SAXS based geometric models (see Appendix A) to (1) predict PMT titration trends and 2) to deconvolve the nominal pore size and material wall-thickness from SAXS data (Scheme 2.1). This approach greatly alleviates the tedious SEM measurements used in our prior studies,\textsuperscript{13,24} and is of particularly utility for large series of samples. The models were derived for a variety of cubic morphologies as well as a generalized form for paracrystals with disordered. These models interpret the first SAXS peak location as a descriptor of the micelle-to-micelle spacing (Scheme 2.1). The
corresponding SAXS d-spacing is scaled by an arbitrary structure factor that is easily obtained by comparison of real and reciprocal space measurements:

\[ S \frac{d_{m-m}}{d_{spacing}} = \frac{q d_{m-m}}{2\pi} \]  

(eq 1)

where \( S \) is the morphology scalar ratio, \( d_{m-m} \) is the micelle-to-micelle spacing determined by real space measurements such as SEM and \( q \) is a well-defined SAXS feature originating from the structure factor.

Figure 2.5 The d-spacing of sample series W7.5 (a, all 3 trials) was fitted from a limited dataset that included SEM measurements from a single sample W7.5-1.13 (solid circle) and all SAXS data (open circles). The interpreted micelle-to-micelle spacing was deconvolved into the template diameter (b) and material wall-thickness (c) based upon the fit from this reduced dataset. The PMT titration curves (dotted lines) were compared to SEM measurements that were excluded from the fitting information (orange triangles). The MCT model was used with the fit parameters identified in Table A.6.

This approach allows geometric in-plane modeling to proceed independent of knowledge of the specific space group. Geometric lattice models allow the prediction of PMT titration curves for trends of d-spacing, template diameter (constant) and wall-thickness with changing M:T ratio. The model uses several fitted terms corresponding to relative densities (\( \beta \)), lattice distortion (\( \Upsilon \)), and a correction for nominal wall orientation distribution (\( \alpha \)). Two classes of template-material interactions were considered separately.
A whole micelle templating (WMT) model assumes that the material is fully phase separated from the micelle template. The WMT model was used to estimate trends in wall-thickness in a prior study.\textsuperscript{13} The micelle core templating (MCT) model assumes that the material mixes with the micelle corona and is phase separated from the micelle core, consistent with prior studies by Xiao et al.\textsuperscript{55} The MCT model also uses separate density terms for each polymer block as well as a volume fraction term for the relative proportions of each block. This later volume fraction term is easily determined based in \textsuperscript{1}H NMR and available homopolymer density values. For both WMT and MCT, the density terms were combined into a single $\beta$ parameter to simplify fitting. The underlying assumptions of these models are 1) a proportional relationship of the SAXS d-spacing to $d_{m-m}$. Therefore, a constant morphology is required for application of the models where morphology symmetry changes would change the relationship of structure factor to the underlying $d_{m-m}$, thus changing $S$. And lastly, 2) the densities of each component are assumed to be constant. The template or pore diameters were calculated using Appendix A equation 21 for the WMT model and Appendix A equation 20 for the MCT model. The predictive power of these SAXS based models was demonstrated by comparing predicted PMT titration curves to measured SEM data (Figure 2.3, Figure A.9, Table 2.4). Of course, a PMT titration curve is only reasonably of use within the PMT window. Both models yielded good fits within the PMT region with d-spacing predictions having $R^2$ values of 0.949 and 0.953 for MCT and WMT models, respectively. The nominal pore diameter calculated from SEM measurements was used as a proxy for the nominal template diameter. Both models yielded good prediction of pore dimensions within the PMT window. Also, both models yielded good predictions of wall-thickness within the PMT.
window with \( R^2 \) values of 0.923 and 0.922 for MCT and WMT, respectively. Subsequent DSC and WAXS data evidenced only amorphous PEO, however, most consistent with the MCT model where the material interacts with the corona and suppresses PEO crystallization (Figure A.6). Thus, the subsequent discussions are focused on the MCT model alone.

The use of geometric models also allows the \( d_{m-m} \) derived by SAXS to be deconvolved into the nominal pore size and material wall-thickness. The MCT interpretation of measured SAXS data identified the unexpected decrease in pore size for sample W7.5-2.07 (Fig 2.3c). Thus the trends identified by the MCT interpretation of SAXS data correctly identify the transition from persistent micelles to dynamic micelles at \( M:T=2.0 \). Far beyond the PMT window, however, the MCT interpretation of SAXS data has little correlation to SEM sample measurements. This is likely correlated to the changing character of the SAXS data for W7.5 samples with \( M:T\geq 2.42 \) and a bimodal character for \( M:T=2.66 \) (Fig 2.3a). This observation suggests a change of morphology symmetry that breaks the model assumptions. We present in Figure 2.6 the trend in scalar S values determined for the W7.5 series. The value of S was relatively constant with some scatter, supporting the model assumption of constant morphology.

The SAXS based model was also used to predict the material wall-thickness. The wall-thickness is expected to vary with lattice orientation, where several examples are provided in the Appendix A (eq 22-24). The wall-thickness is also expected to vary with direction relative to the substrate due to the uniaxial compression that occurs during film casting.\textsuperscript{13,21-22,50,56-57} We focus here exclusively on the in-plane sample dimensions for simplicity. An additional fit term, \( \alpha \), was added to account for the average of a generic
distribution of crystallographic orientations (Appendix A eq 25). This model was examined by comparing the MCT interpreted wall-thickness from SAXS data to the experimentally observed wall-thickness determined using SEM (Figure 2.3d). Others have used GISAXS modeling\textsuperscript{58} to determine pore diameter distribution with form factor fitting. In contrast, our model is independent of symmetry and is conceptually based on conservation of volume.

![Graph showing Scalar, S (unitless) vs. M:T Ratio](https://via.placeholder.com/150)

Figure 2.6 Both WMT and MCT models assume a proportional relationship of SAXS d-spacing to the underlying micelle-to-micelle spacing. The presence of such a constant scalar, S, was examined by comparing SEM and SAXS data dimensions for sample series W7.5.

The MCT best fit parameters are presented in Table 2.5. The density-related $\beta$ value for the MCT model was 4.755. Assuming bulk densities for PEO and PHA, this $\beta$ value corresponds to a material density of 0.36 g cm\textsuperscript{-3}, considerably lower than typical estimates of sol density.\textsuperscript{13,21} This unexpectedly low apparent material density is consistent with the material crosslinking as a result of condensation before complete removal of the solvents (THF and water). Here THF is known to coordinate to metal oxides and water is readily physisorbed. The particularly high-water content needed to suppress chain exchange...
between micelles is expected to concentrate through THF evaporation and could reasonably result in a larger than expected material volume that corresponds to this apparent density obtained by fitting. Please note that the model naturally accounts for retained solvent volume by yielding a low apparent material density. This occurs because the M:T ratio does not account for additional species such as water or THF that occupy volume without contributing towards the M-mass component. For this sample, and all others fitted with either model, best fits were consistently obtained with \( \Upsilon = 1.0 \), corresponding to a simple cubic primitive lattice. The best fit \( \alpha \) value was 0.98, corresponding to a nominal wall-thicknesses that closely corresponds to \( d_{m-m-d_{pore}} \). The MCT model was applied to a constrained dataset to demonstrate prediction with minimal electron microscopy data. A dataset consisting of SEM measurements on a single sample, W7.5-1.13 and a complete SAXS titration dataset were fit with the MCT model (Figure 2.5, Table A.5). This constrained dataset allowed the quantitative prediction of lattice expansion with a \( R^2 \) of 0.942. Similarly, the PMT titration curve for wall-thickness predicted from a constrained dataset had good agreement with the available SEM data, yielding an \( R^2 \) value of 0.939. Thus, we anticipate that SAXS based geometric models will significantly expedite the study of PMT phenomena.

**PMT Window for Low Water Conditions**

The MCT model was applied towards a low water content solution to identify changes to the PMT window. A series of samples were prepared using 1.5 wt% water and material precursors were titrated as described above. After fitting, the MCT interpretation of the SAXS data predicted template/pore diameters that were within 3% of the SEM measurements (Figure 2.7). The PMT window was identified over a limited range of
M:T<1.45. This reduced PMT window is expected when 1) the addition of material reduces the water content by hydrolysis and 2) the starting water content was reduced. These effects combine to present a quickly reduced $\chi_{\text{PHA-solution}}$ that is unable to inhibit micelle diameter changes in response to changing solution conditions. Notably, the W7.5 series is the first extension of PMT to the <25 nm pore diameter regime.\textsuperscript{13} The use of such low molar mass BCP, e.g. KLE polymers,\textsuperscript{11} favors the production of dynamic micelles since the barrier to rearrangement is scales with $(\chi_{\text{PHA-solution}}-0.5)N_{\text{PHA}}$.\textsuperscript{27} The results of sample series W7.5 and W1.5 are thus consistent with the anticipated energetic landscape governing the formation of persistent micelles vs dynamic micelles.

![Figure 2.7 SEM measurements of samples W1.5-1.11 (a) and W1.5-1.48 (b) were used with a series of SAXS measurements to establish MCT fit parameters. The template diameters were deconvolved from the micelle-to-micelle spacing (c) to track changes with M:T.](image)

We anticipate that simple combinatorial mixing strategies could considerably accelerate the preparation of high-resolution M:T series. For example, a solution of persistent micelles (T) and a solution of material sol particles (M) could be dispensed with
Table 2.3 Experimental data from trial 1 of sample series W7.5, including SAXS and SEM measurements as well as the calculated morphology scalar S.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>SAXS Measurements</th>
<th>SEM Measurements</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d-spacing (nm) (^a)</td>
<td>Pore Size (nm)</td>
<td>Wall-Thickness (nm)</td>
<td>(d_{m-m}) (nm)</td>
<td>S, scalar (unitless)</td>
</tr>
<tr>
<td>W7.5-1.13</td>
<td>21.69</td>
<td>12.43±0.01</td>
<td>1.46</td>
<td>6.74±0.03</td>
<td>1.51</td>
</tr>
<tr>
<td>W7.5-1.21</td>
<td>22.30</td>
<td>13.15±0.03</td>
<td>2.75</td>
<td>6.79±0.05</td>
<td>2.27</td>
</tr>
<tr>
<td>W7.5-1.39</td>
<td>22.45</td>
<td>12.31±0.02</td>
<td>1.98</td>
<td>7.26±0.03</td>
<td>1.49</td>
</tr>
<tr>
<td>W7.5-1.46</td>
<td>23.35</td>
<td>13.12±0.01</td>
<td>1.74</td>
<td>7.56±0.04</td>
<td>1.09</td>
</tr>
<tr>
<td>W7.5-1.58</td>
<td>23.94</td>
<td>12.87±0.01</td>
<td>2.26</td>
<td>7.72±0.04</td>
<td>2.22</td>
</tr>
<tr>
<td>W7.5-1.77</td>
<td>24.44</td>
<td>12.30±0.02</td>
<td>1.89</td>
<td>8.96±0.07</td>
<td>2.17</td>
</tr>
<tr>
<td>W7.5-1.94</td>
<td>25.13</td>
<td>13.02±0.01</td>
<td>2.01</td>
<td>9.30±0.09</td>
<td>2.28</td>
</tr>
<tr>
<td>W7.5-2.07</td>
<td>23.38</td>
<td>10.12±0.02</td>
<td>1.99</td>
<td>10.02±0.05</td>
<td>2.37</td>
</tr>
<tr>
<td>W7.5-2.24</td>
<td>25.45</td>
<td>10.14±0.02</td>
<td>1.83</td>
<td>9.46±0.08</td>
<td>1.71</td>
</tr>
<tr>
<td>W7.5-2.3</td>
<td>24.91</td>
<td>10.38±0.02</td>
<td>1.63</td>
<td>10.85±0.07</td>
<td>1.94</td>
</tr>
<tr>
<td>W7.5-2.42</td>
<td>26.72</td>
<td>9.58±0.02</td>
<td>2.21</td>
<td>12.69±0.19</td>
<td>3.09</td>
</tr>
<tr>
<td>W7.5-2.47</td>
<td>26.87</td>
<td>9.49±0.01</td>
<td>1.37</td>
<td>11.89±0.07</td>
<td>2.23</td>
</tr>
</tbody>
</table>

\(^a\)d-spacing calculated by \(2\pi/q\) using the first scattering peak at low-q. \(^b\)Average value ± the error of the mean.

Table 2.4 The MCT model (based on best fit SEM data) predicted and resulted d-spacing, average pore diameter, and wall thickness of “Aged” and “calcined” films varied by M:T ratios, prepared using 7.5w% water.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>PMT Titration Curve (MCT Model)</th>
<th>MCT Interpretation of SAXS Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d-spacing (nm)</td>
<td>Pore Size (nm)</td>
</tr>
<tr>
<td>W7.5-1.13</td>
<td>21.54</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-1.21</td>
<td>21.94</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-1.39</td>
<td>22.80</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-1.46</td>
<td>23.12</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-1.58</td>
<td>23.64</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-1.77</td>
<td>24.42</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-1.94</td>
<td>25.09</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-2.07</td>
<td>25.57</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-2.24</td>
<td>26.17</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-2.30</td>
<td>26.40</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-2.42</td>
<td>26.79</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-2.47</td>
<td>26.95</td>
<td>12.74</td>
</tr>
</tbody>
</table>
variable flow rate ratio using two syringe pumps to access a range of M:T values. The output solutions could be combined with a simple mixing nozzle before continuous application to a substrate via e.g. doctor blading. We envision that such a strategy could enable the production of higher resolution M:T series in a fraction of the time as compared to the manual method employed here.

Table 2.5 MCT model parameters for sample series W7.5 established by a combination of direct measurements and data fitting.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0.98$^a$</td>
</tr>
<tr>
<td>$\beta$ density</td>
<td>4.7549$^a$</td>
</tr>
<tr>
<td>PEO volume fraction</td>
<td>38%$^b$</td>
</tr>
<tr>
<td>$S$</td>
<td>0.8963$^c$</td>
</tr>
<tr>
<td>$\Upsilon$</td>
<td>1.00$^a$</td>
</tr>
<tr>
<td>$g$ Pore size (nm)</td>
<td>12.74$^d$</td>
</tr>
</tbody>
</table>

$^a$ determined by least squares fitting within PMT window
$^b$ calculated with NMR measurements of polymer and bulk homopolymer densities
$^c$ average $S$ value for all samples within PMT window
$^d$ average pore data for all samples within PMT window.

**Tips and tricks**

Many experimental details were scrutinized rigorously for reproducible experiments. We have collected a set of tips and tricks to help new comers avoid common errors. Similar suggestions have been noted elsewhere, where we hope this compilation will help others continue this work. We suggest the following for polymer synthesis:

The preparation of macroinitiators by esterification is sensitive to water contamination. Thus, efforts should be made to maintain the dryness of each reagents. We were able to reproducibly prepare macroinitiators using fresh PEO-OH without further drying. However, repeated openings of the container allow the hygroscopic PEO to uptake atmospheric water. Less-pristine PEO-OH could be used after further drying e.g. by drying in a vacuum oven or by azeotropic distillation of toluene.
The removal of inhibitor from PHA monomer is based on adsorption by passing the as-received monomer through basic activated alumina. Alumina is quite hygroscopic and reduces its efficacy of adsorption with excessive exposure to air. Fresh activated alumina is consistently reliable for inhibitor removal from monomer. Moist alumina may be reactivated with a suitable heat treatment.

Monomer is not long-term stable in the absence of inhibitor. The polymerization reaction should be started within an hour of removing inhibitor from monomer.

The ATRP of PHA may be conducted under numerous conditions. A table of metal-ligand complexes we have used for PHA are provided in Table A2. Very active ligands such as Me₆TREN should be used with lower concentrations than less active ligands such as HMTETA.⁵⁹

It is important to remove oxygen from the polymerization solution before starting ATRP. For demonstration of low-capital synthesis, the experimental procedures reported here used nitrogen sparging. If available, a repeated freeze-pump-thaw sequence is preferable since there is minimal loss of reagents to evaporation. We suggest the following for film synthesis.

Substrate cleaning has a significant effect on reproducibility.⁶⁰⁻⁶¹ In this study, we opted for bench-top cleaning with Piranha solution. Piranha solution is composed of three parts of conc. sulfuric acid (H₂SO₄) and one part of 30% hydrogen peroxide (H₂O₂) solution. The substrates were immersed in pre-heated H₂SO₄ at 80°C for 15 min in a glass crystallization dish. Then desired amount of H₂O₂ was added dropwise since the mixing is quite exothermic. Please note that this Piranha solution is quite hazardous and can react
violently if the H₂O₂ is added too quickly. The solution was then allowed to cool to room temperature and the substrates were rinsed thoroughly with DI water and dried on a hotplate set to 100°C. The cleaned substrates were used for the next step immediately without storage. We have noted that air-borne contaminants will coat substrates within a day. Substrate cleaning by calcination to 400°C for 1 h did not yield as reproducible of results.

The first step of the PMT fabrication is the preparation of a micelle solution. We have found that inhibitor-free, anhydrous THF gives the most reproducible results. The polymer should be fully dissolved in THF before proceeding to micellization. The HCl(aq) was added dropwise without pause between drops. We have noted a pronounced effect of the addition rate of HCl(aq) on the resulting micelle diameters, probably because the micelles become kinetically trapped when the local concentration of water increases heterogeneously.

The entrapment of micelles is dependent on solution water concentrations. Thus, the dryness of the polymers used has an effect on the apparent PMT window. A fully dried state is easiest to reproduce with polymer being dried by heat and high vacuum overnight just prior to use.

Hydrochloric acid (HCl) is important to stabilize many oxide nanoparticle chemistries. The concentration of HCl (aq) decreases with repeated openings of the container. HCl can be transferred to numerous smaller vials to limit the total number of openings for each aliquot. HCl(aq) that was concentrated enough to be visibly fuming when open was sufficient for reproducibility.
The materials precursors are often air sensitive. The niobium ethoxide used here degrades on contact to humidity. The best practice is to transfer such precursors under inert atmosphere, either by using a glovebox or air-free syringe techniques.

The homogenization of persistent micelles with SIE is sensitive to time and temperature. We carefully monitored the 5 min sonication time and always started the process with the water bath equilibrated to room temperature. Please note that some sonication baths are prone to forming standing waves where various positions in the bath have different sonic power.

The titration of material to micelle solutions is sensitive to ambient humidity and should be conducted to exclude as much air as feasible. Micelle solutions were thus prepared in vials with either Teflon-lined caps or rubber septa to allow the introduction of material precursors via air-free syringe. Please note that aluminum lined caps will quickly corrode and contaminate the micelle solution.

The relative humidity (\%RH) during spin coating is important for sample reproducibility. We recommend the flow-controller based setup described in the experimental section to provide stable and continuous air of constant temperature and humidity. Simple needle valves with a floating ball suffice for affordable control of air flows. Also, a commercial aquarium stone is suitable for production of the wet-air stream. Calibration of the relative humidity is also important. Please note that digital hygrometers are prone to rapid corrosion in the presence of HCl, giving rise to erroneous readings. A mason hygrometer is resistant to acids and is a reliable method to validate older digital hygrometers.
The loading of samples into the spin coater necessarily introduces ambient air. A purge time of at least 2 min was used before each coating. The minimum purging time for any setup may be calculated based on purge dilution equation, the container volume, the flow rates, and the acceptable residual concentration of ambient air. Coating with different relative humidity values was found to widely vary the results (Figure A7).

The as-spin coated films were found to change after several days of storage. This is not surprising since the PEO and PHA components are mobile at room temperature and the sample may not be under controlled humidity in the lab. Thus, samples should be promptly transferred from the spin coater to a hot plate to commence the aging process. The aging process cross-links the material and prevents morphology changes over time.

Stray sample solutions can accumulate in the spin coater and distort the resulting morphology trends. The humidity control chamber on the spin coater was thus rigorously wiped clean and flushed with compressed air for 1 min to remove all traces of THF and HCl in between each sample.

The spin speed may obviously be used to modulate the film thickness. The important consequences thereof are multifold. Thicker films increase the SAXS signal and can enable significantly faster measurements for large sample series. Thicker films also undergo slower humidity exchange with the atmosphere. Changes to the spin rate will likely need further adjustments to the relative humidity for the production of well-defined morphologies. To ensure the preservation of morphology through the entire depth of ~570 nm film, cross-sectional SEM measurements were performed (Figure A3). It showed that
despite the noted uniaxial compression, the in-plane pore diameter values were same as the surface up to the M:T<2.0, after which the thicker walls occlude the view of the pores.

The edges of spin coated films exhibited shifted scattering patterns, presumably due to film thickness differences from drying effects. A SAXS map (Figure A8) with 25 measurements across a 6 mm x 6 mm area of a W7.5-1.19 sample showed the sample to be homogeneous with a d-spacing of 21.95 nm and a standard deviation of 0.145 nm. It follows that samples intended for device studies should be prepared in a larger format so that the edges may be discarded.

2.5 Conclusion

Simple SAXS based geometric models were developed to significantly expedite the identification of the PMT windows from SAXS datasets for different solution conditions. The models quantitatively predicted the nominal template/pore diameters as well as the wall-thicknesses. The described one-pot titration-approach enabled markedly faster and more efficient production of continuously varied material:template ratios. These approaches yielded the first PMT window for a low molar mass block copolymer with 12-13 nm mesopores. Lastly, the accelerated synthesis from custom polymer fabrication through micelle templating was demonstrated within 24 h.

2.6 References


CHAPTER 3

EXPANDED KINETIC CONTROL FOR PERSISTENT MICELLE TEMPLATES

WITH SOLVENT SELECTION\textsuperscript{2}

Sarkar, A.; Evans, L.; Stefik, M. \textit{Under Review}, 2018\textsuperscript{2}
3.1 Abstract

The precision control of nanoscale materials remains a challenge for the study of nanostructure-performance relationships. Persistent micelle templates (PMT) are a kinetic-controlled self-assembly approach that decouples pore and wall control. Here, block copolymer surfactants form persistent micelles that maintain constant size as material precursors are added, despite the shifting equilibrium micelle dimension. Prior PMT demonstrations were based upon solvent mixtures where kinetic rates were adjusted with the amount of water cosolvent. This approach is however limited since ever-higher water contents can lead to secondary porosity within the material walls. Herein, we report an improved method to regulate PMT kinetics via the majority solvent. This enables a new avenue for expansion of the PMT window to realize templated materials with a greater extent of tunability. In addition, we report a new SAXS-based log-log analysis method to independently test micelle templated series for consistency with the expected lattice expansion with increasing material:template ratio. The PMT window identified by log-log analysis of SAXS data agreed well with independent SEM measurements. The combination of improved micelle control with solvent selection along with SAXS validation will accelerate the development of a myriad of nanomaterial applications.

3.2 Introduction

The controlled self-assembly of surfactants\(^1\) and block copolymers (BCPs) has led to a wide range of demonstrated feature sizes in porous materials\(^2\) that are applicable to numerous electrochemical devices.\(^\text{13,16,19-20}\) Generally, amphiphilic BCPs are combined with material precursors e.g. metal salts and the combination is organized via evaporation-induced self-assembly where the material selectively associates with one polymer block,
often poly(ethylene oxide). Despite great developments with the number of accessible compositions and morphologies, the simple independent adjustment of pore or wall dimensions while holding the other constant has remained elusive. This challenge has persisted due to the widespread use of equilibrium-based approaches where each feature dimension is subject to the “tyranny of the equilibrium”. Kinetic-based approaches such as Persistent Micelle Templates (PMT) overcome this limitation by using kinetically-trapped (i.e. persistent) micelles that do not change their size during changes to the solution conditions, e.g. the addition of material precursors. The PMT concept thus separates the formation of a fixed micelle dimension from the templating of material precursors. PMT was recently combined with a one-pot titration of material precursors to enable continuously adjustable wall dimensions. Since all measurements of electrochemical performance convolve multiple transport processes, it is crucial to broadly realize independent control of each feature dimension to deconvolve concomitant processes. Furthermore, the realization of a clearly-defined and predictive synthesis approach opens new opportunities to realize nano-optimized devices where each transport pathway is fully optimized for performance.

The precision control of template materials relies upon precision control of the micelle template. Micelle formation is driven by solvent selectivity where the solvophobic blocks aggregate to form micelle cores, each surrounded by the corresponding solvophilic corona blocks. The equilibrium diameter of a micelle results from the balance of interfacial enthalpy with the entropy associated with chain stretching, as well as other terms. In contrast, the actual diameter of a micelle is a combination of the processing history and the kinetics of chain exchange, in addition to the above thermodynamic considerations. For
example, the rate of single chain exchange between micelles is well studied\textsuperscript{27-37} where the rate scales with a double-exponential function of the energetic barrier to chain exchange, $\chi N$ or $f(\chi)N$.\textsuperscript{38} Here, $N$ scales with the molar mass of the solvophobic-core block, $f$ is a monotonic function, and $\chi$ is the effective interaction parameter that embodies the enthalpy associated with interface formation but also includes some non-combinatorial entropy.\textsuperscript{39} Please note that in this context, the relevant $\chi$ term is for the interaction of the core block with the solvent. Thus, high-$\chi N$ conditions can lead to considerably slower exchange rates where micelles become kinetically trapped.\textsuperscript{40} Such kinetically trapped micelles are the basis of PMT where the high-$\chi N$ barrier to chain exchange maintains a constant micelle diameter during the addition of material precursors.\textsuperscript{25-26,41} To date, all PMT demonstrations have relied upon water content alone to regulate $\chi$ within THF-rich solutions. With that limited approach the achievement of persistent micelle conditions with low molar mass polymers is particularly challenging where a large volume fraction of water would be needed for sufficiently high-$\chi N$ conditions. This approach would however cause other deleterious effects during film processing such as secondary porosity within the material walls, \textit{vide infra}. We present here a method to significantly increase $\chi$ during PMT processing via rational solvent selection. A small-angle X-ray scattering (SAXS) based geometric model was previously shown to well-fit persistent micelles during a titration of material precursors.\textsuperscript{26} There, a natural outcome of constant template size and increasing wall material was a quasi-cube root dependence of d-spacing on the material:template ratio. However, that approach required the input of real-space electron microscopy measurements to enable fitting. Here we present a new based upon a log-log coordinate
space that is independent of other measurements and enables the direct testing of SAXS data for consistency with PMT lattice expansion.

### 3.3 Experimental

**Materials**

Anhydrous, inhibitor free tetrahydrofuran (THF, 99%, Aldrich) and niobium(V) ethoxide (99.9%, Fisher) were stored inside a glove box and used as received. Ethanol (EtOH, 200 proof, 100%, Fisher) and methanol (MeOH, 99.8%, Fisher) were dried at room temperature with storage over 50% w/v of molecular sieves (3Å, 8-12 mesh, Acros Organics) for a week.\(^{42}\) 37% w/w conc. HCl (ACS grade, VWR), poly(ethylene glycol)methyl ether (PEO-OH, \(M_n = 5000\) gmol\(^{-1}\), Aldrich), 2-bromopropionic acid (>99%, Aldrich), and 4-(dimethylamino) pyridine (99%, Aldrich) were used as received. The ligand, tris-(2-dimethylaminoethyl) amine (97%, Aldrich) and catalyst, copper(I) bromide (99.99%, Aldrich) were stored inside a glove box and used as received. Hexyl acrylate (96%, VWR) monomer was passed through basic alumina column just before use. Chloroform (>99%, Aldrich), hexane (>98.5%, Fisher) and dimethylformamide (97%, Aldrich) were used as received.

**Polymer Synthesis and Characterization**

A poly(ethylene oxide-\(b\)-hexyl acrylate) diblock copolymer was used in this study and termed OH. The OH polymer was synthesized by a two-step procedure using a steglich esterification followed by atom transfer radical polymerization (ATRP). Polymerization procedure was described elsewhere in detail.\(^{26}\) The molar mass of the PHA was determined by comparison to the PEO using a Bruker Avance III HD 300 \(^1\)H NMR. The molar mass dispersity (D) was characterized by a Waters gel permeation chromatography (GPC)
instrument equipped with a 515 HPLC pump, a 2410 refractive index detector, and three styrage columns (HR1, HR3 and HR4 in the effective molecular weight range of 0.1-5, 0.5-30, and 5-600 kgmol$^{-1}$, respectively). THF was used as eluent at 30 ºC temperature and with a flow rate of 1 mLmin$^{-1}$. The GPC was calibrated with polystyrene standards (2570, 1090, 579, 246, 130, 67.5, 34.8, 18.1, 10.4, 3.4, 1.6 kgmol$^{-1}$) obtained from Polymer Laboratories. GPC samples were prepared in THF with a concentration of 2-5 mgml$^{-1}$ and were filtered through 0.2 μm filter media just prior to injection.

**Micelle Preparation and Measurements**

Solutions were prepared using 100 mg of dried OH polymer in 10 mL of dry solvent, either THF, EtOH, or MeOH at room temperature. The polymer readily dissolved in THF, however, more time and mild shaking 16-20 hours were needed for polymer dispersion in alcohols. Next, aqueous HCl was added dropwise to a total of 200 µL, i.e. 1.96 vol% for all solutions. The resulting micelle solution was sonicated for 5 min at room temperature to enable chain exchange under kinetically limited condition. Dynamic light scattering (DLS) measurements of micelle hydrodynamic diameter were obtained using a Zetasizer Nanoseries ZEN3690 instrument. Solutions for DLS measurement were prepared with OH at a concentration of 10 mgml$^{-1}$. All measurements were run at least 3 times to confirm reproducibility. For DLS analysis the viscosities of 0.455 cP, 1.04 cP, 0.547 cP and refractive indices of 1.409, 1.361, and 1.326 were used for the three solvents, THF, EtOH and MeOH, respectively. The obtained size distributions were well fit with a gaussian function for each peak. The corresponding fitted peak center(s) and standard deviation(s) were reported.
**Micelle Templating**

The formed micelles were then used to template materials using a titration approach. A predetermined amount of niobium ethoxide was added under near air-free conditions, followed by minor agitation and spin coating. This procedure was repeated to produce samples across a range of material:template (M:T) ratios. Here the M:T mass ratio compares the anticipated final oxide mass (Nb$_2$O$_5$) to the polymer mass. Each aliquot was spin coated for 20s at 1000 RPM under 15%RH as described in detail elsewhere.$^{26,43}$ Both glass coverslips and silicon wafers were used as substrates. Immediately after spin coating, each sample was removed from the humidity-controlled chamber and placed on a hot plate for 30 minutes at 200 °C for coverslip glass and 8-12 hours at 100 °C for silicon substrates, respectively, to crosslink the material, termed as “aging”. The longer aging period for silicon substrates was used since those samples were next calcined to 500 °C to remove the polymer for SEM imaging. After each coating the spin coating chamber (Tupperware) was replaced to avoid solvent residues and improve reproducibility.

**X-ray Measurements**

X-ray experiments were conducted using a SAXSLab Ganesha at the South Carolina SAXS collaborative (SCSC). A Xenocs GeniX 3D microfocus source was used with a copper target to produce monochromatic beam with a 0.154 nm wavelength. The instrument was calibrated just before measurement, using the National Institute of Standards and Technology (NIST) reference material, 640c silicon powder with the peak position at 2θ = 28.44 °, where 2θ is the total scattering angle. A Pilatus 300k detector (Dectris) was used to collect the two-dimensional (2D) scattering pattern with nominal pixel dimensions of 172x172 µm. The SAXS data were acquired with an X-ray flux of ~4.1
M photon per second incident upon the sample and a detector-to-sample distance of 1040 mm. Transmission SAXS data were measured to observe the purely in-plane morphology. The 2D images were azimuthally integrated to yield the scattering vector and intensity. Peak positions were fitted using custom MATLAB software. SAXS measurements were reported as the average ± the standard deviation. The error bars for log scale were approximated as 0.434 times the relative error.

**Scanning Electron Microscopy (SEM)**

Top-view images of calcined films were acquired with a Zeiss Ultraplus thermal field emission SEM using an acceleration voltage of 5 keV and an in-lens secondary electron detector. The working distance was maintained at ~3 mm as well as a constant magnification of 400k. Hundreds of measurements were made on each sample to yield statistically significant metrics of pore diameter, and wall-thickness. Data are presented as average values with the error-of-the-mean. Samples with particularly thick walls visually occlude the view of the interior pore diameters and yield pore measurements that are smaller than the actual pore dimensions. With this challenge in mind, a wall: pore ratio was defined as a metric to exclude untrustworthy pore measurements. Here pore size measurements by SEM were considered reliable only if the wall:pore ratio was 0.75 or less.

**3.4 Results and Discussion**

**Thermodynamic Considerations and Solvent Selection**

Persistence, that is the lack of chain exchange between micelles, is a quintessential aspect of PMT. Persistence is maintained by using high-$\chi_N$ solution conditions that suppress chain exchange. Hildebrand solubility parameters ($\delta$) provide a semi-quantitative method to interpret changes to $\chi$ as being proportional to the square of the separation of
two $\delta$ values. Here, the relevant $\chi$ parameter for single chain exchange is between the core block and the solvent mixture. The solubility parameter of solvent mixtures is simply the sum of each solubility parameter weighted by respective volume fraction. Prior demonstrations showed predictive power with THF-water solutions and various molar mass PEO-$b$-PHAs. However, the solubility parameter of THF ($18.5-19.53 \text{ MPa}^{0.5}$) is quite similar to that of PHA ($16.64 \text{ MPa}^{0.5}$). This small separation of solubility parameters implies that the $\chi$ between PHA and THF is expected to be quite small and prior studies detected only unimers for PEO-$b$-PHA in THF without observable micelles (unpublished). Thus, both the micellization and the maintenance of persistent micelles in THF rely upon sufficient water content to raise $\chi$. PMT with low molar mass polymers is particularly challenging where a large volume fraction of 8.09% water was needed for PMT processing. This approach however has limited extensibility since further increases to $\chi$ with water addition lead to the deleterious formation of secondary porosity within the material walls (Figure B.1). Here we instead rationally select alternative solvents based on solubility parameters to enhance $\chi$ and slow chain exchange kinetics (Scheme 3.1).

![Scheme 3.1 Solubility parameters guide the identification of high-$\chi$N conditions to form Persistent Micelle Templates.](image)

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The design of an ideal solvent for PMT is influenced by numerous considerations. 

1) The above thermodynamic considerations suggest that $\chi$ and thus micelle persistence may be enhanced by selecting solvents with higher Hildebrand solubility parameters that increase the solubility parameter separation between the core block and the solvent. For example, MeOH ($\delta\sim29.7$ MPa$^{0.5}$) and EtOH ($\delta\sim26.2$ MPa$^{0.5}$) are considerably more separated from PHA than THF. 

2) The material precursors, often a metal oxide sol, must be soluble in the processing solvent. Hydrogen bonding is one of the most prolific mechanisms for the selective association of sols with the corona block. It follows that solubility of the sol nanoparticles within the solvent often relies upon the possibility to also hydrogen bond with the processing solvent. Thus, ethers and alcohols have been extensively employed elsewhere for the solution processing of sols with block copolymers.

3) The polymer itself must also be dispersible in the processing solvent, an aspect that is subtly distinct from simply being soluble. Solubility is predictable by selecting solvents with similar solubility parameters to a particular polymer block. The hazard of selecting a solvent that is good for both blocks is that the block copolymer may be dispersed as unimers without aggregating to form micelles. To target micelle formation, the processing solvent should be good for the corona block and poor for the core block. Solvation of the corona is critical for micelle dispersion. 

4) For evaporation induced self-assembly, such as PMT, the solvent boiling point and processing conditions of the films must also be considered. Excessively high boiling points $\sim140$ °C take considerable time to dry after spin/dip coating. This extended time period makes the maintenance of kinetic control more difficult where regulation of humidity and temperature must be further optimized. In contrast, solvents with too low of boiling points tend to yield less
homogeneous films. Finally, within the context of maintaining high-$\chi$ conditions one must consider the trajectory of mixed-solvent compositions during evaporative processing. Many ethers and alcohols form an azeotrope with water and can lead to concentration/removal of water depending on the details. 5) Finally, the substrate wetting by the processing solution is significantly tuned by the solvent composition. Often substrate surface energies are not ideally matched to the used solvents where slow evaporation can lead to dewetting and the formation of nanostructured islands rather than a continuous film. The issue of wetting is also often addressed by modification of the substrate surface e.g. with plasma cleaning or functionalized silane coatings, depending on the nature of the substrate-solvent pair. When ideal solvents satisfying all these parameters are not feasible then further care is needed to maintain kinetic control throughout processing.

**Micellization of OH in Different Solvents**

A hallmark sign of dynamic (non-persistent) micelles is the presence of free unimers in solution. This stable unimer population enables continuous exchange of chains between micelles, supporting equilibration. Simple laboratory DLS measurements provide a direct method to probe for the presence of unimers, with typically a hydrodynamic diameter $<10\text{nm}$.\textsuperscript{47-50} A custom OH polymer was prepared and is summarized in Table 3.1 with data presented in Figure B.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_{\text{n,PEO}}$ (gmol$^{-1}$)</th>
<th>$M_{\text{n,PHA}}$ (gmol$^{-1}$)</th>
<th>Total $M_{\text{n}}$ (gmol$^{-1}$)</th>
<th>$\bar{D}$</th>
<th>$f_{\text{PEO}}$</th>
<th>$f_{\text{PHA}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>5,000</td>
<td>9,800</td>
<td>14,800</td>
<td>1.10</td>
<td>0.34</td>
<td>0.66</td>
</tr>
</tbody>
</table>

\(a\) obtained from $^1\text{H}$ NMR analysis, \(b\) obtained from GPC analysis, \(c\) volume fractions (f) calculated using bulk densities\textsuperscript{25,51} PHA = 1.065 gcm$^{-3}$ and PEO = 1.064 gcm$^{-3}$. 

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Three solvents were selected in order of increasing solubility parameter and increasing $\chi$: THF, EtOH, and MeOH. The OH polymer was dispersible in all 3 solvents. DLS measurements of OH in pure THF was largely consistent with unimers and low-number aggregates with perhaps a trace of micelles (Figure 3.1a). Similarly, DLS of OH in EtOH was consistent with unimers or low-number aggregates, suggesting a weakly aggregated system with significant exchange dynamics. The presence of unimers rules out pure THF or pure EtOH as solvents capable of suppressing chain exchange. In contrast, OH in pure MeOH was consistent with full micellization and undetectable aggregates/unimers <10 nm in diameter. Here the absence of detectable unimers suggests MeOH as a good candidate for suppressed chain exchange kinetics. The sol-gel processing of many materials uses acidic aqueous conditions, so the above 3 solutions were measured again after the dropwise addition of 1.96 vol% water via HCl(aq). DLS of each of the 3 solvent mixtures, OH-THF-HCl, OH-EtOH-HCl, and OH-MeOH-HCl were consistent with full micellization without detectable unimers (Figure 3.1b). Here the addition of water is expected to increase the Hildebrand solubility parameter of the solvent mixtures, increasing the effective $\chi$ value between the core block and the solvent mixtures. This increase of $\chi$ is expected to reduce the critical micelle concentration and drive free unimers to join micelles. The detection of unimer-free micelles is a necessary condition for PMT processing where the control mechanism relies upon kinetically hindered chain exchange between micelles. Please note that while this condition is necessary, it may not be sufficient due to the limited sensitivity of DLS towards <10 nm objects. There was some correlation between solubility parameter and hydrodynamic diameter with lowest-$\chi$ solvent THF.
yielding the smallest micelles and the higher-χ solvents EtOH and MeOH yielding larger micelles.

Figure 3.1 DLS measurements of OH polymer dispersed in neat THF, EtOH and MeOH (a), then after addition of HCl(aq) (b) and followed by sonication for 5 min (c).

In equilibrium, the micelle size should increase with χ, however one must also consider kinetics. After HCl(aq) addition, the lack of observable unimers suggests kinetically trapped micelles that are unable to equilibrate on the experimental time scale. Thus, the micelle dimensions are likely a result of their processing history convolving shifting thermodynamics and slowing kinetics during the addition of water. Lastly, we note that DLS measures the hydrodynamic diameter that includes both the micelle core and corona in addition to the sphere of solvation. However, the template pore dimensions are
expected to be dependent upon the micelle core alone.\textsuperscript{26} The homogenization and size adjustment of kinetically trapped micelles poses obvious challenges. Next, the micelle solutions were subjected to sonication induced exchange (SIE) for 5 min.\textsuperscript{41} Here sonication enables switchable exchange between micelles where they return to a kinetically trapped condition upon the cessation of cavitation. SIE shifted the nominal hydrodynamic diameters and slightly narrowed the size distributions for the alcohol-water mixtures (Figure 3.1c, Table 3.2). We speculate that the largest hydrodynamic diameter observed for micelles in EtOH was partially attributed to extension of the corona chains. Subsequent micelle templating indicated that the micelles prepared from EtOH and MeOH had nearly identical micelle core dimensions, \textit{vide infra}. All DLS results are summarized in Table 3.2.

The OH micelles prepared with different solvent mixtures were next used to template materials.

Table 3.2 Summary of DLS measurements of OH in different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>OH + Solvent</th>
<th>OH + Solvent + HCl(aq)</th>
<th>OH + Solvent + HCl(aq), 5 minutes sonication</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>1.86±0.31</td>
<td>20.71±4.54</td>
<td>21.14±4.58</td>
</tr>
<tr>
<td></td>
<td>5.88±0.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.43±2.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>5.82±1.13</td>
<td>43.31±9.17</td>
<td>38.63±8.36</td>
</tr>
<tr>
<td>Methanol</td>
<td>16.71±3.52</td>
<td>38.08±7.38</td>
<td>28.78±5.42</td>
</tr>
</tbody>
</table>

**Independent Test of SAXS Consistency with PMT Model**

Determination of PMT processing conditions has remained cumbersome. We recently reported a geometry-based SAXS model\textsuperscript{26} that deconvolves scattering data into the underlying pore and wall dimension based upon fit parameters and additional input
from real-space measurement such as SEM. This model assumed the simple conservation of volume to calculate the expanding lattice dimensions as material is added to micelle templates. One of the core outcomes of this model is the nearly cube-root dependence of d-spacing on the material:template ratio (M:T). This dependence is a natural outcome from the cubic dependence of unit cell volume upon the lattice dimension. This approach allows for comparison of plots of d-spacing vs material:template ratio to be compared to a PMT model. Deviations from the model may be caused by breaking any of the underlying assumptions such as: (1) changes to template size from loss of micelle persistence (Figure 3.2a red), (2) changes to the material or template density (Figure 3.2a yellow), or (3) change of structure factor (Figure 3.2a).

Figure 3.2 Simulated SAXS data for films with increasing Material:Template ratios are expected to yield an expanding lattice when the micelle template is persistent (a). A modified coordinate space would ideally allow independent validation of SAXS consistency with PMT lattice expansion when the slope is 1/3 (b). An equivalent coordinate space is proposed based on an approximation to enable independent validation of SAXS consistency with the PMT model (c). Deviations from the model are depicted for each plot. This new tool rationally constrains model fitting to the apparent PMT window (c).

Logarithmic manipulation of the generalized formula (Appendix B, Eq S3) results in a predicted PMT model (Figure 3.2b, blue) having a constant slope of 1/3 on a graph of \( \log(d\text{-spacing}) \) vs \( \log(x\beta_{\text{mct}}+1+(f_{\text{corona}}/(1-f_{\text{corona}}))) \), where \( x \) is the M:T ratio, \( \beta_{\text{mct}} \) is a convolved density term, and \( f_{\text{corona}} \) is the volume fraction of the corona block (Figure 3.2b).
Analysis within this coordinate space is ideal where PMT series yield a slope of 1/3 even under changes to the sol density. However, the $\beta_{mct}$ term on the X-axis is the result of SAXS fitting and is thus generally unknown until the fit region is constrained. Since the M:T ratio is generally between 1-3, $\beta_{mct}>4$, and $f_{corona}<0.4$, one may approximate $(x\beta_{mct}+1+(f_{corona}/(1-f_{corona})) \approx x\beta_{mct}$ (Appendix B, Eq S4). Further log rearrangements yield a more utilitarian coordinate space where log(d-spacing) vs log(M:T) should also maintain a slope of 1/3 during the predicted PMT lattice expansion (Appendix B, Eq S5). This latter criterion provides an improved test for PMT conditions from SAXS-alone and without input from real-space measurements (Figure 3.2c). Here we note that the elimination of $\beta_{mct}$ in this simplified coordinate space will only provide a slope of 1/3 if: (1) the template diameter is constant, (2) the $\beta_{mct}$ convolved density parameter is constant, and (3) the structure factor relationship to d-spacing is constant. With this new tool in hand, we examine the capability of THF, EtOH, and MeOH to enable materials prepared from persistent micelle templates.

**Micelle Templating in THF (lowest-\(\chi\))**

We examine the effect of solvent selection on a PMT titration starting from the lowest anticipated $\chi$ examined: a THF solution with 1.96 vol% water (Scheme 3.1). A one-pot titration approach was used where material precursors were stepwise added to the micelle solution and nanomaterials were prepared by spin coating aliquots. Here niobium ethoxide was the material precursor used to prepare niobium pentoxide. For clarity, a single representative sample, OH-THF-1.40, is first presented before elaborating the series of THF samples (Figure 3.3). Here the SAXS data exhibited two isotropic scattering peaks with an approximate q-ratio of 1:2 (Figure 3.3a), suggestive of limited ordering such as
randomly packed spheres. Additionally, the SEM data (Figure 3.3b) exhibits short-range ordering where template mesopores (dark) were seen in niobium oxide (bright). The d-spacing from the first SAXS peak (d*=2π/q) closely matched the d_{m-m} measured from SEM images and was most consistent with disordered sphere packing. Thus, the previously reported paracrystalline PMT SAXS model was used for the series.

Figure 3.3 Characterization of sample OH-THF-1.40 by SAXS (a) and SEM (b). The isotropic 2D SAXS pattern is inset in (a) where the color scale corresponds to the log of X-ray intensity. The momentum transfer q=4πsin(θ)/λ where 2θ is the total scattering angle and λ is wavelength.

Three titration series were conducted and the SAXS data for series 1 are presented in Appendix B, Figure B.3, where the first maximum monotonically moves to lower-q, corresponding to an increasing d-spacing (d=2π/q) from lattice expansion. Replotting the scattering data into the simplified log-log coordinate space identified a limited region from the start of the titration to M:T~1.56-1.68 where the titration series all followed lattice expansion with the expected slope of 1/3 (Figure 3.4a), indicating consistency with the PMT model. All samples in OH-THF-Series3 had ~5% smaller d-spacings and were attributed to a reduced nominal micelle dimension (Figure 3.4b), presumably as a result of
the micellization procedure. Both statistical variation within individual samples and variation between repeated series were used to inform subsequent analysis. Variation within individual samples in OH-THF-Series1 were quantified with 9 SAXS measurements at different positions on each sample. This variation was minor with typically 1-4% across each sample for M:T<1.55. For M:T>1.55, variation within samples increased significantly and was attributed to the micelles becoming appreciably dynamic. The significantly widened statistical distribution upon the apparent exit of persistent micelles, however inhibits the use of error bars alone to identify consistence with PMT lattice expansion.

Figure 3.4 Analysis of micelle templates processed from a THF solution. The d-spacings obtained from the principal scattering peaks were plotted in a log-log coordinate space to identify consistency with PMT lattice expansion when the slope is 1/3 (a). The identified region was fitted with a PMT SAXS model (b). The average pore size was calculated from independent SEM measurements to confirm the PMT region by a second method (c).
The departure of the nominal d-spacing values from a slope of 1/3 on the log-log plot as well as the significantly increased variation across individual samples identified a PMT window from M:T=1.26 to M:T~1.56-1.68. This variability in PMT window is perhaps not unexpected since the transition from persistent to dynamic micelles is expected to be a continuum where evidence of dynamic exchange requires both sufficient rate and time and are likely temperature sensitive. Based on the identified PMT window, the constrained SAXS dataset and subsequent SEM measurements (Figure 3.4c, Figure B.4, Table B.1) were used to fit the PMT model to OH-THF-Series1 and OH-THF-Series2 resulting in a goodness of fit $R^2=0.798$ (Figure 3.4b). The resulting fit parameters are shown in Table 3.3.

Table 3.3 Fit parameters for PMT titration series in different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Pore Diameter (nm)$^a$</th>
<th>$S$ (unitless)$^c$</th>
<th>$\alpha$ (unitless)$^b$</th>
<th>$\beta$ (unitless)$^b$</th>
<th>$\gamma$ (unitless)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>12.36</td>
<td>0.963</td>
<td>0.90</td>
<td>5.47</td>
<td>1.00</td>
</tr>
<tr>
<td>EtOH</td>
<td>11.84</td>
<td>0.997</td>
<td>0.89</td>
<td>5.65</td>
<td>1.00</td>
</tr>
<tr>
<td>MeOH</td>
<td>12.94</td>
<td>1.047</td>
<td>0.85</td>
<td>7.07</td>
<td>1.00</td>
</tr>
</tbody>
</table>

$^a$obtained by averaging SEM measurements $^b$obtained by least squares fitting. $^c$average structure factor $S$ obtained by comparing SEM and SAXS measurements.

This PMT window is also consistent with the trend in average SEM pore diameter measured for OH-THF-Series1, that was relatively constant in the region identified as having persistent micelles where the pore size decreased by 0.7 nm (~6% change) at M:T=1.53. Transition from persistent to dynamic micelles for OH-THF-Series1 determined by SEM was nearly the same (2% difference) as that determined by the log-log SAXS analysis, highlighting both the accuracy and utility of the log-log method. This limited PMT window is expected since the water that maintains micelle persistence is consumed by hydrolysis of the niobium pentoxide precursor. A simple stoichiometry
calculation indicates that all water could be consumed by hydrolysis near M:T=1.72, ignoring condensation. This indicates that the THF solvent system requires an appreciable amount of water to maintain persistent micelles. The d-spacing results were quite varied in the dynamic micelle regime, exhibiting significant variability with different series. Variations in titration speed and room temperature may contribute to this scatter as micelles become observably dynamic. In conclusion, a modest PMT window just 0.2 ΔM:T wide was identified using THF with 1.96 vol% water.

**Micelle Templating in EtOH (moderate-χ)**

The effect of solvent selection on PMT is next examined with a moderate anticipate χ condition: an EtOH solution with 1.96 vol% water. The earlier DLS measurement of OH in pure EtOH exhibited a population of unimers like THF, indicating that EtOH is also expected to lead to dynamic micelles when anhydrous. For ethanol samples, the SAXS measurements again generally exhibited 2 peaks with a ratio of ~1:2 and the SEM images contained only short-range ordering, consistent with disordered sphere packing (Figure B5). Several titration series were conducted and the SAXS data from OH-EtOH-Series1 are presented as Figure B6. The determined peak positions were converted and presented as d-spacing vs M:T. Again, the log-log coordinate space was employed to identify the window of micelle persistence for fitting (Figure 3.5a). The EtOH series followed the expected slope of 1/3 for PMT lattice expansion until a transition region from persistent to dynamic micelles was identified M:T~2.18-2.42, depending on the specific titration series. The combined dataset for OH-EtOH-Series1 and OH-EtOH-Series2 were fit using the same paracrystalline model and yielded a goodness of fit R²=0.972 (Figure 3.5b) in this region. This was similar to the region identified by direct SEM measurements of pore diameter.
distributions (Figure 3.5c, Table B2) where the average pore diameter dropped from 11.84 nm to 10.43 nm (~12% change) for M:T=2.06 in OH-EtOH-Series1. Again, comparison of the identified PMT region determine by SEM and log-log SAXS analysis had good agreement for the same series (5% difference). In comparison with the THF data above, the EtOH data clearly demonstrates that increased \( \chi \) enables expansion of the PMT window. In other words, the reliance upon the concentration of water as a co-solvent is reduced to lower critical value for maintaining micelle persistence in EtOH. In comparison to THF, the EtOH series had significantly reduced variation across samples in both the persistent and dynamic regions. Surprisingly, the average pore diameter measured by SEM initially decreased and then increased with further titration into the dynamic micelle regime, M:T=2.11-2.51. The previous stoichiometry consideration indicates that the solution may have become anhydrous in this regime. The trajectory for \( \chi \) changes is not clear in this regime, however the SEM data suggest that \( \chi \) increases with further material addition. In comparison to THF, a 3 times wider PMT window 0.68 \( \Delta M:T \) was identified for EtOH, consistent with the larger \( \chi \) value.

**Micelle Templating in MeOH (highest-\( \chi \))**

Lastly, the effect of solvent selection on PMT was examined for the solvent having the highest anticipated \( \chi \), MeOH. Notably, MeOH was the only solvent in this study where DLS measurements indicated both the presence of micelles and an undetectable presence of free-unimers in the pure, anhydrous solvent. The same 1.96 vol% water was used to maintain similar sol-gel chemistry as the other solvent mixtures examined here. Multiple titration series were carried out and the SAXS profiles for OH-MeOH-Series1 are shown in Figure B.7. Like the other solvents, the MeOH series all increased in d-spacing with
material additions and these data were plotted in a log-log coordinate space where the lattice expansion with titration followed the expected slope of 1/3 through M:T~2.15-2.40 (Figure 3.6a).

Figure 3.5 Analysis of micelle templates processed from an EtOH solution. The d-spacings obtained from the principal scattering peaks were plotted in a log-log coordinate space to identify consistency with PMT lattice expansion when the slope is 1/3 (a). The identified region was fitted with a PMT SAXS model (b). The average pore size was calculated from independent SEM measurements to confirm the PMT region by a second method (c).

Again, the variability in PMT exit point was attributed to a continuous transition from persistent to dynamic micelles that is sensitive to time and temperature. The SAXS profiles again consisted of 2 peaks with an approximate 1:2 q-ratio and the SEM images contained short and medium range ordering. Notably the samples processed from MeOH exhibited improved ordering and contained limited regions with 2-fold and 4-fold
symmetry (Figure 3.7). The combined 3 MeOH series were fitted within the apparent PMT window using the same paracrystalline PMT model and yielded a goodness of fit $R^2=0.932$ (Figure 3.6b). Separate consideration of the SEM data alone indicated a similar PMT window with a relatively constant average pore size of 12.94 nm until a decrease to 12.75 nm at M:T=2.07 for OH-MeOH-Series1 and a continued decrease to 12.44 at M:T=2.16 (~4% decrease). Again, the PMT region identified by SEM and log-log analysis were in close agreement (4% difference). Curiously, the average pore size initially decreased in the dynamic region and then later increased, similar to the EtOH series (Figure 3.6c, Table B.3). Here both the SAXS and SEM data indicate that OH does not form persistent micelles in pure-MeOH, but rather requires a small portion of water to be present. Also, the Nb$_2$O$_5$ wall-thickness was increased monotonically from 6.24 to 9.33 nm during material titration and followed the PMT model with $R^2=0.974$ (Figure 3.6d). Compared to THF, the increased $\chi$ from using MeOH significantly expanded the PMT window to 0.84 $\Delta$M:T. However, in comparison to EtOH, the switch to MeOH resulted in a similar PMT exit point, within the uncertainty of the methods. A possible explanation is that the $\chi$ change when switching from EtOH to MeOH was not as large as estimated from solubility parameters (Scheme 3.1). The overall trends highlight a significant role of solvent selection upon $\chi$ and the PMT processing window.
Figure 3.6 Analysis of micelle templates processed from a MeOH solution. The d-spacings obtained from the principal scattering peaks were plotted in a log-log coordinate space to identify consistency with PMT lattice expansion when the slope is 1/3 (a). The identified region was fitted with a PMT SAXS model (b). The average pore size was calculated from independent SEM measurements to confirm the PMT region by a second method (c). The average wall thickness was also measured by SEM and compared to model predictions (d).

Figure 3.7 SEM images of OH-MeOH-Series1 in order of increasing Material:Template ratio, 1.23 (a), 1.50 (b), 1.60 (c), 1.68 (d), 1.73 (e), 1.83 (f) 2.07 (g), and 2.39 (h).

3.5 Conclusion

In this work the effect of solvent selection on PMT kinetic-control was guided by solubility parameter considerations. Simple DLS measurements confirmed the presence of OH unimers in pure-THF and pure-EtOH, confirming the presence of dynamic micelles. In contrast DLS of OH in MeOH was consistent with micelles alone with undetectable unimers. Also, a new log-log analysis technique was developed based upon SAXS data alone to test for sample consistency with the PMT model of lattice expansion. The
combination of this analysis with a one-pot titration-approach enabled efficient confirmation of PMT conditions before further measurements and model refinement. The PMT exit point was expanded by selecting solvents with higher solubility parameters. Using a constant 1.96vol% of water, PMT control with THF spanned up to M:T~1.5, with EtOH up to M:T~2.0, and with MeOH up to M:T~2.1. The findings highlight a new avenue to tune the processing window of persistent micelle templates. Continued development in this direction may enable future PMT processes from simple single-solvent systems. These developments support the predictable synthesis of highly tunable nanomaterials that are important for a wide range of applications.

3.6 References

7. Crepaldi, E. L.; Soller-Illia, G. J. de. AA.; Grosso, D.; Cagnol, F.; Ribot, F.; Sanchez, C. 

8. Tate, M. P.; Urade, V. N.; Gaik, S. J.; Muzzillo, C. P.; Hillhouse, H. W. *Langmuir*


10. Chen D.; Li, Z.; Wan, Y.; Tu, X.; Shi, Y.; Chen, Z.; Shen, W.; Yu, C.; Tu, B.; Zhao,


     **2011**, *133*, 6513-6516.

     1802–1809.


18. Fried, D. I.; Ivanova, A.; Muller, V.; Rathousky, J.; Smarsly, B. M.; Fattakhova-

19. Peters, K.; Lokupitiya, H. N.; Sarauli, D.; Labs, M.; Pribil, M.; Rathousky, J.; Kuhn,


Sarkar, A.; Thyagarajan, A.; Cole, A.; Stefik, M. *Manuscript in Preparation.* Preliminary data are presented here.
4.1 Abstract

Persistent micelle templating (PMT) demonstrated the systematic control of architectural dimension in the porous materials that is not feasible under equilibrium. Prior works demonstrated the achievement of broader ranges of mesopores with tunable wall-thickness, that is limited by synthesis of various block copolymers. To overcome this challenge, a pore swelling approach under kinetic control is presented here. It leads to the use of fewer polymers that needed to cover a wide range of length scales of both pore size and wall-thickness tunability from a single polymer. Pore swelling approach was developed employing a custom-made polymer, poly(ethylene oxide-block-hexyl acrylate), homopolyhexylacrylate (h-PHA) as a swelling agent and a high $\chi$ solution condition for entrapping the micelles. Pore sizes were tuned continuously in the range of 15-35 nm and 40-60 nm from a smaller and larger sized block copolymer and varying ratio of swelling agent. However, excess addition of swelling agent cannot be homogeneously mixed with micelle core and phase separate that results into formation of foam-like disordered porous structure. Maintenance of kinetic control was demonstrated also tuning wall-thickness with the expanded pores. This approach improves the PMT fabrication with varying range of pore sizes with controlled tunability where minimum polymer synthesis is required.

4.2 Introduction

Mesoporous, crystalline inorganic oxide materials derived from block copolymer structure directing agent attracted a lot of attention due to their high surface-area, large pore volume and potential application in structure-property and performance relationship in electrochemical studies. The preceding chapters demonstrate how the newly developed persistent micelle templating (PMT) could enable the systematic control of architectural
dimension in the porous materials \(^{13-15}\) which is not feasible under equilibrium.\(^{16-18}\) PMT is based on the entrapment of kinetically frozen micelles that are employed in the template fabrication with tunable architectural dimensions. The major requirements of PMT include a custom-made block copolymer, Poly(ethylene oxide-\textit{block}-hexyl acrylate) PEO-\textit{b}-PHA, and a mixed solvent-system that can establish a high-\(\chi_N\) solution condition and inhibit the polymer chain exchange between micelles.\(^ {13,15}\) Prior works demonstrated the achievement of materials with broader range of mesopores (13-80 nm) with tunable wall-thickness (6-58 nm) within a single morphology\(^ {13-15}\) which was discussed in Chapter 2. A conceptual framework needed to realize PMT \(\leq 10\) nm had also been discussed in detail in Chapter 3. However, attainment of the broader ranges of pore size with tunable wall-thickness is a cumbersome process and limited by various block copolymers with different molar masses as each pore size demands a specific molar mass. To overcome this, a pore expansion agent is used to change the micelle diameter by swelling its core selectively.\(^ {19-21}\) This approach results into the uses of fewer polymers that needed to cover a wide range of micelle core size. Novelty of this introduced approach is the swelling of PEO-\textit{b}-PHA micelle core by hydrophobic homopolymer while kinetic control is maintained. This idea was established by demonstrating the tunability of wall-thickness while the pore sizes remain constant. This approach not only reduces the synthetic effort, it also covers a wide range of length scales of both pore size and wall-thickness tunability from a single polymer with a single sol-gel recipe.

Herein, we report a variable range of pore sizes employing a single PEO-\textit{b}-PHA (14,737 g mol\(^{-1}\)) as a template under a high \(\chi\) (methanol-3.5 w\% water) solution condition. A low-molecular-weight homopolyhexylacrylate (h-PHA) (913 g mol\(^{-1}\)) was used as a pore-
expander. Due to the smaller size and hydrophobic nature, h-PHA can easily solubilize into micelle core and increase the core diameter. The pore sizes were tuned in the range of 15-35 nm by adding various amount of swelling agent (0-500%) into the micelle. However, excess addition (>250%) of h-PHA cannot be homogeneously mixed with micelle core and phase separate that results into formation of foam-like disordered porous structure. Therefore, uncontrolled micelle swelling can generate macropores although order and homogeneity of the templated pore system compromise. The pore expansion with different concentration of swelling agent was demonstrated combining transmission SAXS and SEM. Moreover, wall-thickness tunability with the expanded pore was demonstrated for the first time employing the PMT concept. This approach improves the PMT fabrication with varying range of pore sizes with controlled tunability where minimum polymer synthesis is required.

4.3 Experimental

Materials

Anhydrous, niobium(V) ethoxide (99.9%, Fisher) was stored inside a glove box and used as received. Methanol (MeOH, 99.8%, Fisher) was dried at room temperature with storage over 50% w/v of molecular sieves (3Å, 8-12 mesh, Acros Organics) for a week. 37% w/w conc. HCl (ACS grade, VWR), poly(ethylene glycol)methyl ether (PEO-OH, Mn = 5000 gmol⁻¹, Aldrich), 2-bromopropionic acid (>99%, Aldrich), methyl-2-bromopropionate (98%, Aldrich) and 4-(dimethylamino) pyridine (99%, Aldrich) were used as received. The ligand, tris-(2-dimethylaminoethyl) amine (97%, Aldrich) and catalyst, copper(I) bromide (99.99%, Aldrich) were stored inside a glove box and used as received. Hexyl acrylate (96%, VWR) monomer was passed through basic alumina column
just before use. Chloroform (>99%, Aldrich), hexane (>98.5%, Fisher) and
dimethylformamide (97%, Aldrich) were used as received.

**Polymer Synthesis and Characterization**

A poly(ethylene oxide-b-hexyl acrylate) diblock copolymer was used in this study
and termed OH_1. The OH_1 was synthesized combining two-step procedure using a
steglich esterification followed by atom transfer radical polymerization (ATRP).
Polymerization procedure was described elsewhere in detail.\(^\text{15}\) A homopolyhexylacrylate
(h-PHA) was synthesized by ATRP using a reagent ratio of [hexyl acrylate]:[2-
ethylbromopropionoate]:[Me\textsubscript{6}TREN]:[Cu(I)] = 50:1:0.5:0.5. To a Schlenk flask, 332 μL
of 2-ethylbromopropionoate initiator was mixed with 22.7 mL of inhibitor free hexyl
acrylate monomer. The flask was capped with rubber septa, tightened with copper wire and
sparged with nitrogen gas for 1 h to remove dissolved oxygen. A catalyst stock solution of
1 mL of toluene containing 91 mg Cu(I)Br and 355 μL (0.5 mmol) Me\textsubscript{6}TREN ligand was
added to the reaction flask under flowing N\textsubscript{2} gas. This reaction mixture was then placed
into a pre-heated oil bath at 70 °C with constant stirring. The polymerization was continued
for 50 mins. The reaction mixture was cooled before exposing the solution to air. The crude
polymerization solution was diluted with THF and passed through a basic alumina column
to remove copper salts. The product was precipitated into 5-fold excess of cold methanol
(-78 °C), using a dry ice-acetone bath). The collected polymer was dried using rotovap.
The polymers OH_1 and h-PHA were characterized by NMR and GPC. The molar mass
of the PHA was determined by comparison to the PEO using a Bruker Avance III HD 300
\(^1\)H NMR. The molar mass dispersity (D) was characterized by a Waters gel permeation
chromatography (GPC) instrument equipped with a 515 HPLC pump, a 2410 refractive
index detector, and three styrigel columns (HR1, HR3 and HR4 in the effective molecular weight range of 0.1-5, 0.5-30, and 5-600 kgmol\(^{-1}\), respectively). THF was used as eluent at 30 °C temperature and with a flow rate of 1 mLmin\(^{-1}\). The GPC was calibrated with polystyrene standards (2570, 1090, 579, 246, 130, 67.5, 34.8, 18.1, 10.4, 3.4, 1.6 kgmol\(^{-1}\)) obtained from Polymer Laboratories. GPC samples were prepared in THF with a concentration of 2-5 mgml\(^{-1}\) and filtered through 0.2 μm filter media just prior to injection.

**Micelle Sample Preparation**

Micelle solutions was prepared dispersing 25 mg of dried block copolymer and required amount of h-PHA in 2.5 mL of dry MeOH. The solution was heated at 80 °C for an hour. Please note that heating was used here instead of sonication to enable chain exchange under kinetically limited condition\(^{23}\) and heating step produced a very homogeneous film, evident by SEM (Figure C.9). Exceeding the concentration of h-PHA to 250%, the micelle solution appeared to be very cloudy, suggesting formation of h-PHA aggregates first rather being in single chain and inserts into micelle core. Next, 37w% HCl (aq) was added dropwise into it to a total water content of 3.0 w%.

**Micelle Templating**

Formed micelles with varying concentrations of h-PHA were used to template materials using a titration approach. A predetermined amount of niobium ethoxide was added under near air-free conditions, followed by minor agitation and spin coating. This procedure was repeated to produce samples across a range of material:template (M:T) ratios. Here the M:T mass ratio compares the anticipated final oxide mass (Nb\(_2\)O\(_3\)) to the polymer mass. Each aliquot was spin coated for 20s at 1000 RPM under 15%RH as described in detail elsewhere.\(^{15}\) Both glass coverslips and silicon wafers were used as
substrates. Immediately after spin coating, each sample was removed from the humidity-controlled chamber and placed on a hot plate for 30 minutes at 200 °C for coverslip glass and 8-12 hours at 100 °C for silicon substrates, respectively, to crosslink the material, termed as “aging”. The longer aging period for silicon substrates was used since those samples were next calcined to 600 °C to remove the polymer for SEM imaging.

**X-ray Measurements**

X-ray experiments were conducted using a SAXS Lab Ganesha at the South Carolina SAXS collaborative (SCSC). A Xenocs GeniX 3D microfocus source was used with a copper target to produce monochromatic beam with a 0.154 nm wavelength. The instrument was calibrated just before measurement, using the National Institute of Standards and Technology (NIST) reference material, 640c silicon powder with the peak position at 2θ = 28.44 °, where 2θ is the total scattering angle. A Pilatus 300k detector (Dectris) was used to collect the two-dimensional (2D) scattering pattern with nominal pixel dimensions of 172x172 µm. The SAXS data were acquired with an X-ray flux of ~4.1 M photon per second incident upon the sample and a detector-to-sample distance of 1040 mm. Transmission SAXS data were measured to observe the purely in-plane morphology. The 2D images were azimuthally integrated to yield the scattering vector and intensity. Peak positions were fitted using custom MATLAB software.

**Scanning Electron Microscopy (SEM)**

Top-view images of calcined films were acquired with a Zeiss Ultraplus thermal field emission SEM using an acceleration voltage of 5 keV and an in-lens secondary electron detector. The working distance was maintained at ~3 mm as well as a constant magnification of 400k. Hundreds of measurements were made on each sample to yield
statistically significant metrics of pore diameter, and wall-thickness. Data are presented as average values with the standard deviation.

4.4 Results and Discussion

Synthesis of OH_1 Diblock Copolymer and h-PHA Homopolymer

The block copolymers and h-PHA were prepared and summarized in Table 4.1 with data presented in Figure C.1-C.4. The molar mass of the PHA was determined by $^1$H NMR with the corresponding signals $\delta$ (ppm) for OH_1: 4.0 (COOC\textsubscript{2}H\textsubscript{5}), 2.27 (CH\textsubscript{2}BrCOO), 1.90 (CH\textsubscript{2}CHBrCOO). $^1$H NMR (300 MHz, CDCl\textsubscript{3}), and $\delta$ (ppm) for h-PHA: 4.0 (COOC\textsubscript{2}H\textsubscript{5}), 2.27 (CHBrCOO), 1.90 (CH\textsubscript{2}CHBrCOO), 3.64 (CH\textsubscript{3}CHBrCOOCH\textsubscript{3}). The molar mass dispersity ($\bar{D}$) was determined 1.11 for OH_1, 1.39 for OH_2 and 1.36 for h-PHA respectively. All data suggested monodispersing molecular weight distributions.

Table 4.1 Characteristics of OH polymer used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$, PEO (gmol$^{-1}$)</th>
<th>$M_n$, PHA (gmol$^{-1}$)</th>
<th>Total $M_n$ (gmol$^{-1}$)</th>
<th>$\bar{D}$</th>
<th>$f_{\text{PEO}}$</th>
<th>$f_{\text{PHA}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH_1</td>
<td>5,000</td>
<td>9,737</td>
<td>14,737</td>
<td>1.11</td>
<td>0.34</td>
<td>0.66</td>
</tr>
<tr>
<td>OH_2</td>
<td>20,000</td>
<td>33,417</td>
<td>53,417</td>
<td>1.39</td>
<td>0.37</td>
<td>0.63</td>
</tr>
<tr>
<td>h-PHA</td>
<td>---</td>
<td>1,173</td>
<td>1,173</td>
<td>1.36</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

$^a$ obtained from $^1$H NMR analysis, $^b$ obtained from GPC analysis, $^c$ volume fractions (f) calculated using bulk densities$^{13,24}$ PHA = 1.065 gcm$^{-3}$ and PEO= 1.064 gcm$^{-3}$.

Mesoporous Templates from OH_1

A single representative sample, OH_1-MeOH micelle was prepared by dispersing the block copolymer in dry methanol and kinetically trapped via adding 3.0w% water onto it. The micelle diameter or nominal pore diameter was characterized by SAXS and SEM after templating with niobium ethoxide precursor with the material to template ratio (M:T) of 1.40. The scattering data exhibited two isotropic peaks with an approximate q-ratio of 1:2 (Figure 4.1a), suggesting randomly packed spheres.$^{25}$ Additionally, the SEM data
(Figure 4.1b) supports the fact of packed sphere exhibiting moderate-range order. The primary scattering peak obtained by SAXS showing the d-spacing of 28.2 nm, and micelle-to-micelle spacing ($d_{m-m}$) of 21.2 nm by SEM, that further supports the disordered packing of spheres. The SEM pore size analysis depicts the pore diameter of 15.05 nm with moderate standard deviation of 2.28 nm.

Figure 4.1 OH_1-MeOH sample characterized by SAXS (a) and SEM (b).

**Micelle Core Swelling Under Kinetic Control Using Homopolymer**

In order to get niobium oxide templates with larger pore size, h-PHA of 1,173 gmol$^{-1}$ was used as a pore expander. Please note that other two h-PHA candidates (Table C.1) were not successful to swell the micelle core significantly as they were too large to enter into micelle core. Therefore, minimum of 10-12 times lighter homopolymer w.r.t hydrophobic moiety of block copolymer was considered as the best candidate to swell micelle core. To examine an effect of different homopolymer concentrations on micelle core, a series of different h-PHA concentrations were studied first, summarized in Table 4.2. The OH_1 micelle solution was mixed with h-PHA and kinetically trapped using methanol-water solution. Micelle solutions with different loading of h-PHA were prepared carefully as the homopolymer was aimed to be in single chain and enter into micelle core first, rather not being aggregate and phase separate from micelle core. Failure to do so, h-
PHA forms aggregates and phase separate from micelles, evident by SEM (Figure C.5). The color of the micelle solution is a good indication for that. As the solution becomes cloudier with a very high concentration of h-PHA (>250-500%), the chance of aggregate formation increases (Figure C.6).

Table 4.2 The d-spacing and pore size summary of OH_1 in methanol with variable concentrations of h-PHA.

<table>
<thead>
<tr>
<th>h-PHA_1 concentration in OH_1-MeOH</th>
<th>d-spacing (nm) $^a$</th>
<th>Pore size (nm) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>26.40</td>
<td>15.05±2.28</td>
</tr>
<tr>
<td>20%</td>
<td>29.58</td>
<td>18.21±3.06</td>
</tr>
<tr>
<td>80%</td>
<td>37.05</td>
<td>23.13±2.98</td>
</tr>
<tr>
<td>150%</td>
<td>41.10</td>
<td>24.41±3.88</td>
</tr>
<tr>
<td>250%</td>
<td>47.40</td>
<td>34.88±6.04</td>
</tr>
<tr>
<td>500%</td>
<td>52.04</td>
<td>35.78±8.15</td>
</tr>
</tbody>
</table>

$^a$ obtained from SAXS, $^b$ obtained from SEM, ± represents the statistical measurement, standard of error.

The SAXS patterns (Figure 4.2) for all mesoporous templates synthesized from OH_1 with different amount of h-PHA showed the same scattering patterns with expanded lattice parameters up to the homopolymer concentrations of 250%. Repetition of the same scattering pattern suggests the preservation of the morphology with the changing solution condition and successful entrapment of micelles. However, a change in the structure factor was observed for the 500% h-PHA and continued to be broadening and disappearing of first scattering maximum. This was further observed by SEM where a sponge or foam like structure was found (Figure C.7) that is consistent with distorted domains or partial destruction of mesostructure. Therefore, only up to the 250% addition was considered for studying swollen nanostructures within single morphology (Figure 4.3). Increment of lattice parameters from 26.4 nm to 37.05 nm further suggests pore expansion by adding h-PHA 80%. Also, the SEM validates ~1.6x pore sizes increment for the same mesoporous templates (15nm to 23 nm) with nanostructure retention. Pore expansion observed up to
the addition of 250% except partial destruction of structures were noticed with higher loading of h-PHA (Figure 4.3).

![Figure 4.2 SAXS measurements of OH_1-MeOH samples with varied ratio of h-PHA and a constant M:T=1.40 ratio. The dotted line drawn through the first scattering maximum shows the lattice parameter expansion, where each peak direction shifts to the lower q (nm$^{-1}$) or higher d-spacing (nm). The scattering data were offset vertically for clarity.](image)

![Figure 4.3 SEM images of mesoporous templates prepared by OH_1-MeOH samples with varied ratio of h-PHA with 0% (a), 20% (b), 80% (c), 150% (d), 250% (e) and 500% (f). A constant M:T ratio of 1.40 was maintained here. All the scale bars are set at 100 nm. Moreover, this observation motivates to achieve a broader range of pore sizes in macroporous materials using a heavier polymer, OH_2 and h-PHA mixture in methanol. Employing the pore swelling concept, same ~1.6x pore size increment was achieved where 62.2±18 nm was obtained by swelling the micelle core with 80% h-PHA, which originally](image)
yields 40.5±10.6 nm pore size (Figure 4.4). This further drive us to examine PMT condition on the expanded pore size, discussed in next section.

Figure 4.4 SEM images of macroporous templates prepared by OH_2-MeOH samples (a) and with 80% loading of h-PHA_1 (b). A constant M:T ratio of 1.40 was maintained here. All the scale bars are set at 50 nm.

**Tunability of Architectural Dimension in 80% h-PHA Loaded OH_1.**

Next, tuning of material wall-thickness with constant expanded pore size was investigated. In order to apply the PMT concept, 80% h-PHA rich sample of OH_1 was examined. A titration series was conducted following the procedure described elsewhere. Templates with varying material ratio of 0.7 to 2.6 were examined by SAXS and SEM. Please note that here M:T ratio was calculated based on block copolymer and homopolymer mass. The first scattering peak for each sample monotonically moves to lower-q (Figure C.8), corresponds to an increasing d-spacing (d=2π/q) from lattice expansion. The d-spacing data followed the PMT titration curve up to the M:T ratio of 2.3 and suggests persistency loose at the ratio of ~2.30 (Figure 4.5a). This is further verified by SEM (Table 4.3, Figure 4.6) and depicts the maintenance of constant average pore sizes of ~25 nm throughout the entire M:T range (Figure 4.5b). This suggests the imposing of PMT condition with independent tailoring of wall-thickness where wall-dimension increases from 7 nm to 9 nm (Figure 4.5c) within single morphology.
Figure 4.5 Analysis of micelle templates processed from a 80% h-PHA rich sample. The d-spacings obtained from the principal scattering peaks were plotted and compared with the PMT model data (a). The average pore size (b) and wall-thickness (c) calculated from independent SEM measurements to confirm the PMT region.

Figure 4.6 SEM images of 80% h-PHA rich OH_1 in order of increasing Material:Template ratio, 1.07 (a), 1.46 (b), 1.74 (c), 1.90 (d), 2.03 (e), 2.28 (f), 2.37 (g) and 2.55 (h).

This is encouraging as we were able to achieve ~25 nm constant pore size from 14.7k g mol⁻¹ polymer which originally yielded pore size of ~15 nm. We demonstrated also the tunable architectural control on this new pore size by maintaining kinetic entrapment of frozen micelles. We believe this will open up a new era where minimum polymer synthesis effort is required to obtain various ranges of pore sizes along with tunable wall-thickness.
Table 4.3 Measurements of 80% h-PHA rich OH_1 block copolymer samples.

<table>
<thead>
<tr>
<th>M:T ratio</th>
<th>SAXS d-spacing (nm)</th>
<th>SEM average pore diameter (nm)±standard deviation</th>
<th>SEM average wall thickness (nm)±standard deviation</th>
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<tr>
<td>0.70</td>
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<td>2.60</td>
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</table>

4.5 Conclusion and Ongoing Work

Preliminary results demonstrate a facile approach to cover a wide range of length scales wide tunability of both pore size and wall-dimension from a single polymer with a single sol-gel recipe. This approach was designed based on the swelling of micelles with homopolymer while maintaining kinetic control. A moderate range of homopolymer concentration employed to expand pore sizes 1.6-2 times. This demonstrates use of fewer polymers to cover a large range of architectural dimension. Preliminary data showed the pore expansion from 15 nm to 25 nm by swelling micelle core via 80% homopolymer under kinetic control and achieved from a 14.7k gmol\(^{-1}\) block copolymer. A PMT approach was further employed on the expanded pore, 25 nm, to tune wall-thickness from 7 nm to 9 nm within a single morphology. These motivate us to explore further controlling the swelling agent concentration differently to access larger range of pore size, specifically 3x. This will
enable to have access on a wide range of architectural dimension with minimum synthetic effort.

4.6 References


CHAPTER 5

ROBUST POROUS POLYMERS ENABLED BY A FAST TRIFLUOROACETIC ACID ETCH WITH IMPROVED SELECTIVITY FOR POLYLACTIDE$^4$

5.1 Abstract

Polylactide is a widely used sacrificial block for the preparation of porous polymers from ordered block copolymers. Although numerous etching strategies were developed in the past decade, demonstrations to date are limited by slow etch rates that require as long as a week for the etching of few-mm thick films. Recent studies have also shown that NaOH etching of thin-films can degrade the morphology, highlighting the need for more selective processes. Here we report an aqueous trifluoroacetic acid etchant that results in an enhanced etch rate of 14 nm/s with greatly improved selectivity for poly(styrene-block-lactide). The high etch rate enables the complete removal of polylactide from 2 mm thick block copolymer films in 19 h. Furthermore, the improved etch selectivity enables the macroscopic preservation of morphologies as confirmed by both SAXS and SEM and yields pristine porous PS as confirmed by NMR and GPC.

5.2 Introduction

Mesoporous materials derived from block copolymers are crucial for numerous applications including size selective separations such as ultrafiltration for water treatment,\textsuperscript{1-3} the controlled delivery of drugs,\textsuperscript{4-6} templating of surface patterns,\textsuperscript{7-8} and production of functional inorganic nanostructures.\textsuperscript{9-13} The self-assembly of block copolymers into ordered morphologies provides a scalable approach for the synthesis of ordered materials with uniform, nanoscale pores\textsuperscript{14-19} and high specific surface areas that may be chemically functionalized.\textsuperscript{20-21} The selective etching of a sacrificial block is the most widespread method of producing such porous polymers with polylactide emerging as one of the most widely used sacrificial blocks.\textsuperscript{20-25} Despite numerous etching chemistries for poly(styrene-\textit{b}-lactide) (PS-\textit{b}-PLA) type polymers reported in the literature,\textsuperscript{23-24,26-27}
there remain challenges in balancing the extent of an etch process against the preservation of the nanostructure. For example, a widely used alkaline etch route\textsuperscript{23-24} has been noted to damage the quality of thin-film pattern transfer after 15 minutes of mild 0.05 M NaOH contact, limiting thin film pattern retention to films less than 50 nm.\textsuperscript{27-28} The etching of thick polymer films is also challenging where high selectivity of the etchant is crucial to limit the degradation of the retained PS block while providing enough exposure time to etch through the PLA and across multiple grain boundaries. Etching through <1 mm thick PS-\textit{b}-PLA with 0.5 M NaOH typically requires about 3-5 days, corresponding to an average etch rate of 1-1.5 nm/s.\textsuperscript{12-13,23-24} For example, complete PLA removal from films <0.32 mm thick films required shear alignment of the morphology to reduce the grain boundary concentration and a 44 hr etch with 0.5 M NaOH.\textsuperscript{23}

The preservation of the chemical integrity of the PS matrix is crucial for nanostructure retention through a complete etch process. Here, we note that the ideal evidence for nanostructure retention over macroscopic regions is an ensemble measurement such as SAXS that samples a few mm\textsuperscript{3} to quantitatively confirm the preserved lattice parameters over \(\sim 10^{13}\) unit cells, rather than localized microscopy data.\textsuperscript{12-13,23-24,29-33} There are examples of PS-\textit{b}-PLA\textsuperscript{12} and related poly(norbornylethylstyrene-styrene-\textit{b}-lactide) (PNS-\textit{b}-PLA)\textsuperscript{34} films that exhibited a shift in the SAXS pattern after NaOH etching. Such shifts of SAXS peak positions demonstrate a change to the scattering structure factor and were indicative of morphology shrinkage. Reports of PLA etching to date have yet to demonstrate the complete removal of PLA from ordered films thicker than 0.32 mm while preserving the morphology as confirmed by an ensemble measurement such as SAXS.
An ideal etchant would 1) quickly hydrolyze the PLA backbone while 2) maintaining orthogonality towards other blocks such as PS. Trifluoroacetic acid (TFA) is a widely used agent for hydrolytic ester cleavage in preparative organic chemistry owing to its high acidity (low pKa) and concomitant miscibility with both water and organic solvents. The latter criterion is subtlety important where surface wetting of the resulting hydrophobic PS pores is a crucial factor for etching beyond the perimeter.\textsuperscript{35-36} Despite the remaining challenges for etching PS-\textit{b}-PLA, TFA has not yet been investigated as an etchant for porous polymers. We note that TFA was previously used for hydrolysis of homogeneous solutions of PLA-based block copolymers.\textsuperscript{37} Here, we report a significantly higher etch rate of 14 nm/s using TFA to enable the complete etching of 2 mm thick films in less than 1 day while quantitatively preserving the starting morphology and without observable degradation of the remaining PS.

5.3 Experimental

Materials

Styrene (99\%, Acros Organics) was used after passage through a basic alumina column. 3,6-dimethy-1,4-dioxane-2,5-dione (99\%, Acros Organics) or D,L-lactide was dried overnight in a vacuum oven at 40°C just prior use. 2-hydroxyethyl-2-bromoiodobutyrate (95\%, Aldrich), tris-[2-(dimethylamino)ethyl]amine (97\%, Aldrich), tin(II) ethylhexanoate (92\%, Aldrich), benzoic acid (99.5\%, Aldrich), trifluoroacetic acid (99.5\%, Acros Organics) sodium hydroxide (97\%, pellet, Sigma Aldrich) were used as received. Copper(I) bromide (99.99\%, Aldrich), cylochexylamine (99\%, Alfa Aesar), 3,5-bis(trifluoromethylphenyl isothiocyanate) (98\%, Aldrich), anhydrous chloroform (stabilized with amylene, 99.9\%, Acros Organics) were stored inside a glove box and used
as received. 1,8-diazabicyclo[5.4.0]undec-7-ene (98%, Aldrich) was dried over calcium hydride and then filtered in a glovebox using a nylon syringe filter (0.45 µm). Tetrahydrofuran (99.5%, Macron), methanol (99.8%, BDH), and toluene (99.5%, Macron) were used as received.

Synthesis of Hydroxyl Terminated Polystyrene (PS-OH) macroinitiator

The PS-OH macroinitiator was synthesized via ARGET-ATRP using a reagent ratio of [Styrene]:[2-hydroxyethylbromoisobutyrate]:[Me_6TREN]:[Cu(I)]:[Sn(II)]=300:1:0.105:0.005:0.1. To a schlenk flask, 66 mL of inhibitor free styrene (576 mmol) and 278 µL 2-hydroxy-2-ethylbromoisobutyrate (1.92 mmol) were added. The flask was degassed by three freeze-pump-thaw (FPT) cycles and backfilled with nitrogen (N_2) gas. A catalyst stock solution of 1 mL of toluene containing 1.4 mg Cu(I)Br (0.0096 mmol), 53.8 μL (0.2 mmol) Me_6TREN ligand and 62.2 μL Sn(II) ethylhexanoate (0.192 mmol) were added to the reaction flask under flowing N_2 gas. This reaction mixture was then placed into a pre-heated oil bath with constant stirring. The polymerization was continued for 10 hr and at the end the reaction mixture was cooled with ice water before exposing the solution to air. The crude polymerization solution was diluted with THF and precipitated two times into 10 fold excess of cold methanol. The product was filtered and vacuum dried at 50°C for 24 hr. The number average molecular weight (M_n) of PS-OH was 12.9 kg mol\(^{-1}\) and molar mass dispersity \(\bar{D} = 1.21\) were determined with a PS calibrated GPC.
Synthesis of co-catalyst bis(3,5-trifluoromethyl)phenylcyclohexylthiourea

The ROP co-catalyst was synthesized following a reported procedure. The synthesis was performed in a glovebox where 3, 5-bis(trifluoromethyl)phenylisothiocyanate (3.37 mL, 18.5 mmol) and anhydrous THF (20 mL) were combined in a round bottom flask that was previously dried by heat-gun and contained a magnetic stir bar. In the glovebox, cyclohexylamine (2.11 mL, 18.5 mmol) was added to the stirring solution dropwise via a syringe. The reaction continued at room temperature for 24 hr and then THF was removed using a rotary evaporator. The white residue was recrystallized twice from chloroform and stored in the glove box after drying under vacuum at 50°C for 48 hr.

Synthesis of PS-b-PLA

The PS-OH macroinitiator was chain extended from the terminal hydroxyl group via organocatalytic ROP using a reagent ratio of [PS-OH]:[Lactide]:[DBU]:[Thiourea]=1:250:1.34:1.34. Before starting the reaction, the PS-OH macroinitiator and D,L-Lactide monomer were each dried separately overnight at 40°C under high vacuum before transfer to a glove box via a sealed schlenk flask. The PS-OH (1g, 77.1µmol) and lactide monomer (2.8 g, 19.3 mmol) were combined with thiourea co-catalyst (37 mg, 103 µmol). All the reagents were dissolved in 5 mL of anhydrous chloroform. After dissolution, the DBU catalyst (41 µL, 103 µmol) was added to the polymerization mixture dropwise and the reaction was stirred at RT for 60 min. The reaction mixture was terminated by adding benzoic acid (12.6 mg, 103 µmol). The polymer solution was precipitated twice into 10 fold excess of cold methanol. The white solid was
collected by filtration and dried under vacuum at 40°C for 24 hr. The molar mass was determined to be $M_n = 41.6\, \text{kg/mol}$ with $\text{PLA } M_n = 28.6\, \text{kg/mol}$ (79% monomer conversion), as calculated from $^1\text{H} \text{NMR results. GPC confirmed a narrow molar mass dispersity } D = 1.16$.

**Sample Preparation**

PS-$b$-PLA polymer films were prepared by solution casting from toluene (10 wt% of polymer, filtered through 0.2 µm filter) into a Teflon dish placed on a hot plate set to 50°C. The film was left to dry for 8 hr and then transferred to a vacuum oven set to 40°C for another 2 hr to remove trace solvent. The dried sample was annealed at 110°C for 1 hr in a vacuum oven. The oven was vented to atmospheric pressure and the sample quenched to room temperature. The resulting “as-made” sample was used for subsequent etching experiments.

**PLA Etching by TFA Immersion**

A portion of the as-made film 2 mm in thickness and >1 cm$^2$ in area was immersed in a glass vial containing 10 mL of TFA solution. The sample etch rates were compared by maintaining a constant minimum sample dimension of 2 mm in thickness, see section PLA Etch Kinetics below. TFA etchant solutions were prepared using a range of molarities from 0.01-8M, as prepared in a 70:30 mixture by volume of methanol:water. The vial containing etchant and sample was placed in an oven pre-heated to 40°C for the desired amount of time. After this etch treatment, the film was rinsed thoroughly with water and immersed in methanol for 10 minutes before drying in a vacuum oven set to 30°C for 4 hr. The procedure steps are shown in Figure D.6.
**PLA Etching by TFA Vapor**

A portion of the as-made film 2 mm in thickness and ~ >1cm² in area was placed in an aluminum dish. The same range of TFA etchant solutions were examined for vapor etching. The resulting TFA solution (10 mL) was placed in a glass vial. The aluminum dish and glass vial were both placed within a plastic jar and the entire assembly was placed within an oven pre-heated to 40°C for a predetermined amount of time. After this etch treatment, the film was rinsed thoroughly with water and immersed in methanol for 10 minutes before drying in a vacuum oven at 30°C for 4 hr. The procedure steps are shown in Figure D.7.

**PLA Etching by 0.5 M NaOH**

A portion of the as-made film was immersed in 0.5 M NaOH in a 40:60 mixture by volume of methanol: water and etching was conducted for 3 days at 60°C. After this etch treatment, the film was rinsed thoroughly with water and methanol. The extent of PLA etch and the morphology were monitored by ¹H NMR and SAXS, respectively.

**PLA Etch Kinetics**

The etch rate was determined by monitoring the etching of planar films. Here the minimum film dimension was maintained at 2 mm in thickness. For such an anisotropic shape with an isotropic etchant, the film thickness will largely determine the etch time and allow the estimation of the etch rate by minimizing edge effects. The extent of the PLA removal was monitored using ¹H NMR on portions of film as a function of etch time. The disappearance of the non-convolved PLA proton (Figure 5.4 proton-g) was compared to the non-convolved PS protons (Figure 5.4 protons-a) to quantify the amount of PLA remaining relative to the starting diblock copolymer. The spectra were normalized to have
the a-integral correspond to the 5*DP$_{PS}$ where the PLA remaining was quantified as DP$_{PLA}$=g-integral. The etch rate was calculated using rate(nm$^{-1}$) = (film thickness (nm) x %PLA degraded) / (2 x etching time (s)). This calculation assumes a constant velocity of the etch interface and the factor of 2 accounts for etching from both of the exposed film surfaces. The assumption of linear etch rates was supported by time resolved measurements.

**Molecular Characterization**

All proton nuclear magnetic resonance ($^1$H NMR) and heteronuclear single quantum coherence (HSQC) spectra were recorded on Bruker Avance III HD 300. NMR samples were prepared in deuterated chloroform (CDCl$_3$) at a concentration of ~1 wt%. Molecular weight (Mn) and molar mass dispersity (Ɖ) were determined using a Waters gel permeation chromatography (GPC) instrument equipped with a 515 HPLC pump, a 2410 refractive index detector, and three styragel columns (HR1, HR3, and HR4 in the effective molecular weight range of 0.1-5, 0.5-30, and 5-600 kg/mol respectively). Tetrahydrofuran (THF) was used as the eluent at 30°C at a flow rate of 1 mL/min. The GPC was calibrated with PS standards (2,570, 1,090, 579, 246, 130, 67.5, 34.8, 18.1, 10.4, 3.4, 1.6 kg/mol) obtained from Polymer Laboratories. GPC samples were prepared by dissolving the sample in THF at a concentration of 2.0 mg/mL and were filtered (0.2 μm) just prior to injection.

**Small-Angle X-Ray Scattering (SAXS)**

X-ray scattering experiments were conducted using a SAXSLab Ganesha at the South Carolina SAXS Collaborative. A Xenocs GeniX3D microfocus source was used with a Cu target to generate a monochromatic beam with a 0.154 nm wavelength. The instrument was calibrated using National Institute of Standards and Technology (NIST) reference
material, 640c silicon powder with the peak position at \(2\theta=28.44^\circ\) where \(2\theta\) is the total scattering angle. A Pilatus 300 K detector (Dectris) was used to collect the two-dimensional (2D) scattering patterns with the incident beam normal to the planar sample surface. 2D images were azimuthal integrated to one-dimensional (1D) data of intensity (I) versus q (momentum transfer). All data were acquired after one hr of measurement with an X-ray flux of \(~4.1\) M photons/s incident upon the sample. SAXS data were fit using custom MATLAB software.

**Field Emission Scanning Electron Microscopy (FE-SEM)**

After PLA etching, samples were mounted on brass shims using carbon adhesive (Electron Microscopy Sciences) and imaged normal to the planar film surface. Samples were sputter coated with gold-palladium alloy using a Denton Desk II Sputter Coater with global rotation and tilt to avoid sample charging. Images were acquired using an acceleration voltage of 5 keV with an in-lens secondary electron detector. The working distance was fixed to 3.00 mm or less for the acquisition of the images.

### 5.4 Results and Discussion

A prototypical PS-\(b\)-PLA with a lamellar (LAM) morphology was used for development of etch conditions applied towards \(mm\)-thick films. The polymer was synthesized using sequential polymerization reactions from an initiator with both alkyl halide and alcohol functionalities. ARGET-ATRP\(^{39}\) was used to grow PS from the alkyl halide of the initiator. Subsequently, ROP\(^{38,40}\) was used to grow PLA from the alcohol group of the initiator. The PS-\(b\)-PLA had a molar mass of 41.6 kg/mol and contained 66 vol\% of PLA with a molar mass dispersity (\(\bar{D}\)) of 1.16 (Table 5.1).
Ordered 2 mm thick films of PS-\textit{b}-PLA were prepared by solvent casting, followed by an annealing treatment to yield the “as-made” film. The 2D SAXS pattern of the as-made film consisted of isotropic rings (Figure D.1), indicating a homogeneous distribution of grain orientations with abundant grain boundaries as a worst-case scenario for etching. The scattering profile was consistent with LAM symmetry, having peaks observed at \(q/q^*\)=1, 2, 3, and 4 with a \(d\)-spacing of 33.9 nm. A 2 mm thick PS-\textit{b}-PLA film was etched with TFA solution by direct immersion. The 1 M TFA etch kinetics were monitored by \(^1\text{H}\) NMR by the disappearance of PLA at \(\delta 5.19\) ppm. The TFA immersion etch kinetics were linear (\(r^2=0.98\)) with a best-fit etch rate of 14 nms\(^{-1}\) (Figure 5.1).

Table 5.1 PS-\textit{b}-PLA Characterization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(M_n,\text{PS}) (kg mol(^{-1})) (^a)</th>
<th>(M_n,\text{PLA}) (kg mol(^{-1})) (^b)</th>
<th>Total (M_n) (kg mol(^{-1})) (^c)</th>
<th>(D) (^a)</th>
<th>(f_v^{\text{PS}}) (^d)</th>
<th>(f_v^{\text{PLA}}) (^d)</th>
<th>Morphology (^e)</th>
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<tr>
<td>PS-\textit{b}-PLA</td>
<td>12.9</td>
<td>28.6</td>
<td>41.6</td>
<td>1.16</td>
<td>0.34</td>
<td>0.66</td>
<td>LAM</td>
</tr>
</tbody>
</table>

\(^a\) obtained from GPC analysis, \(^b\) obtained from \(^1\text{H}\) NMR analysis, \(^c\) obtained from \(a+b\) \(^d\) volume fractions \((f_v)\) calculated using densities\(^{24,41}\) at 110\(^\circ\)C, PS= 1.02 g/cm\(^3\), PLA = 1.18 g/cm\(^3\) \(^e\) Morphology determined by SAXS.

Figure 5.1 PLA etch kinetics from PS-\textit{b}-PLA immersed 1 M TFA solution.
The resulting fully etched sample was termed “TFA-etch” (Table 5.2). Sample TFA-etch was stable under ambient conditions and was mechanically rather brittle due to the high Tg of PS. For comparison, 0.5 M NaOH was reported to have an etch rate of 1-1.5 nms\(^{-1}\) at 65°C for <0.5 mm thick film.\(^{23-24}\) Similarly, a dilute 0.05 M NaOH was reported to yield initial etch rates of 0.02 nms\(^{-1}\)\(^9,27,42\) and an average etch rate of 0.6-0.9 nms\(^{-1}\)\(^{43}\) for thin films. Likewise an etch rate of 0.17 nms\(^{-1}\) was found with yet more dilute 0.01 M NaOH.\(^{28}\) Broadly, NaOH etch rates are reported to increase with temperature\(^{23-24}\). For comparison, an as-made film was etched with a popular 0.5 M NaOH etchant at 60°C and was termed “NaOH-etch”.\(^{23-24}\) The PLA was completely removed after 3 days of etching, corresponding to an etch rate here of 3.8 nms\(^{-1}\) (Table 5.2). This etch rate is considerably slower than the 14 nms\(^{-1}\) found with immersion in 1 M TFA at 40 °C, despite the slightly reduced temperature. The morphology before and after etching was compared by SAXS. Measurements of sample TFA-etch (Figure 5.2a) exhibited the same series of highly ordered SAXS reflections, indicating that both the unit cell symmetry and lattice parameters were preserved through the TFA etch. The presence of mesopores is evidenced by the combination of mesostructure preservation (SAXS and SEM) combined with \(^1\)H NMR demonstrating complete removal of the PLA phase. Please note that the effects of different unit cell dimension and symmetry have been looked at extensively elsewhere.\(^9,11,43\) None the less, we also demonstrated 100% PLA removal and complete morphology retention for a hexagonal morphology using the same 1 M TFA etching procedure (Table D.1, Figure D.9). SEM measurements of sample TFA-etch confirmed the preservation of the ordered morphology with a d-spacing of 31.8 ±4.0 nm (Figure 5.2b), consistent with the SAXS findings. The complete removal of PLA by 0.5M NaOH required
significantly longer 3 days exposure to etchant and resulted in morphology degradation evidenced by a few weak SAXS shoulder (Figure D.2). Although NaOH has been widely used successfully to etch thinner <1 mm films, these data suggest that modified conditions may be more efficacious for few-mm thick films. Highly selective etchants are needed to enable the etching of macroscopic films that support large-volume production of nanostructured materials, e.g. catalytic applications. The use of a fast TFA etch implies a shortened exposure to etchant and was demonstrated to preserve the PS nanostructure through the complete removal of PLA from 2 mm thick films (Table 5.2).

Table 5.2 Sample names and treatments applied to 2 mm thick films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Etch Rate (nm/s)</th>
<th>LAM Morphology</th>
<th>d-spacing (nm) (obtained by SAXS)</th>
<th>Observed SAXS reflections (q/q*)</th>
<th>Etch Time (hrs)</th>
<th>Etch Conditions</th>
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<td>As-made</td>
<td>---</td>
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</tr>
<tr>
<td>TFA-etch</td>
<td>14</td>
<td>Preserved</td>
<td>33.9</td>
<td>1,2,4</td>
<td>19</td>
<td>Immersed in 1M TFA</td>
</tr>
<tr>
<td>TFA-etch-vapor</td>
<td>9.5</td>
<td>Preserved</td>
<td>33.1</td>
<td>1,2,4</td>
<td>32</td>
<td>In contact with 8 M TFA vapor</td>
</tr>
<tr>
<td>NaOH-etch</td>
<td>3.8</td>
<td>Degraded</td>
<td>---</td>
<td>---</td>
<td>72</td>
<td>Immersed in 0.5 M NaOH</td>
</tr>
</tbody>
</table>

The selectivity of TFA as an etchant was further examined in terms of PS degradation by both GPC and $^1$H NMR. During synthesis, GPC demonstrated chain extension from the PS-OH macroinitiator to the final PS-$b$-PLA diblock copolymer. After
TFA etching, GPC elugrams exhibited a nearly identical molar mass distribution to that of the parent PS-OH macroinitiator (Table 5.3) and was consistent with 100% PLA removal without observable damage to PS (Figure 5.3). Please note that PS does not contain ester groups is not expected to degrade by hydrolysis during etching.

Figure 5.2 (a) SAXS of as-made PS-\textit{b}-PLA compared to fully etched sample TFA-etch by immersion in 1M TFA. The samples were indexed for LAM symmetry with peaks indicated at \( q/q^*=1, 2, 3, \) and 4 where \( q = 4\pi\sin(\theta)/\lambda \). The lines in (a) were offset vertically for clarity. (b) Top-view SEM image of mesoporous PS in sample TFA-etch.

Table 5.3 GPC characterization of PS-OH macroinitiator, PS-\textit{b}-PLA, and TFA-etch film.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( M_n ) (kg mol(^{-1}))</th>
<th>( D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-OH</td>
<td>13.0</td>
<td>1.21</td>
</tr>
<tr>
<td>PS-\textit{b}-PLA</td>
<td>57.6</td>
<td>1.16</td>
</tr>
<tr>
<td>TFA-etch</td>
<td>13.0</td>
<td>1.20</td>
</tr>
</tbody>
</table>

\( M_n \) (kg mol\(^{-1}\)) and \( D \) obtained by GPC.
Figure 5.3 GPC traces of the PS-OH used to make PS-b-PLA as well as the fully etched sample TFA-etch.

Complimentary $^1$H NMR data also showed complete removal of PLA, proton g at 5.19 ppm, without noticeable change to the PS spectra (Figure 5.4d). Please note that the new peak at 1.5 ppm was attributed to water (Figure 5.4d) and was confirmed to not be associated with the PS carbon by heteronuclear single quantum coherence (HSQC) spectroscopy (Figure D.3). In contrast, the NMR spectra of sample NaOH-etch sample exhibited spectral changes in the $^1$H δ1.0-2.0 ppm range with two new correlated carbon peaks (δ40-44 ppm) by HSQC (Figure D.5, shown by arrow) that may correspond to damage to the PS backbone after the extended etch process needed for 2 mm thick films. We note that the initiator group (proton-d at 3.5 ppm) was removed by both NaOH and TFA etching procedures (Figure 5.4c and 5.4d).

Indeed, bases are industrially used for the deliberate degradation of PS with reported products of styrene, ethyl benzene, toluene, cumene and indane derivative. However, these side products were not observed in the NaOH-etch solution nor rinsates as
examined by $^1$H-NMR. In contrast, HSQC spectra of TFA-etch and PS-OH samples exhibited the same peak correlations without apparent changes to the polymer (Figure D.3 and Figure D.4). TFA was demonstrated to enable remarkable etch selectivity with fast PLA removal and without apparent damage to PS.

Figure 5.4 $^1$H NMR spectra of (a) PS-OH (b) PS-$b$-PLA before etching and samples (c) NaOH-etch and (d) TFA-etch.

Wide ranges of TFA etching conditions were examined. Etching by both direct immersion and vapor exposure were investigated separately with the experimental setups pictured in Figure D.6 and Figure D.7. In both cases, the PLA etch rate increased with TFA concentration where etching by direct immersion was faster than by vapor exposure for a particular TFA molarity (Figure 5.5). Also in both cases, an upper limit of TFA concentration was observed where the ordered morphology was lost, presumably due to plasticization of the glassy PS. For example, immersion in 8 M TFA led to the fastest observed rate of 139 nms$^{-1}$, corresponding to 100% PLA removal in 2 h, however SAXS
indicated collapse of the ordered morphology (Figure 5.5 shown in shaded region). Such a high TFA concentration may plasticize the PS and lead to the collapse of the porous morphology. Optimized conditions enabled the fastest etch rates that preserved the parent morphology. The optimum etch conditions were found to be 1 M TFA for immersion etching and 8 M TFA for vapor etching. The latter optimized 8 M TFA vapor etch was linear ($r^2=0.97$) with a best fit etch rate of 9.5 nm s$^{-1}$ (Figure D.8). Considering the absence of liquid solvent, the observed linear kinetics are surprising since the resulting pores are expected to be filled with lactic acid until the later rinse step. SAXS and SEM measurements also confirmed morphology preservation of TFA-etch-vapor after complete PLA removal (Figure 5.6).

![Etch rates with varying TFA concentration by either immersion or vapor exposure.](image)

**Figure 5.5** Etch rates with varying TFA concentration by either immersion or vapor exposure. The etch rates were calculated after a 24 hr etch at 40°C, except for 1 M TFA immersion and 8 M TFA vapor where PLA was completely removed in less time. SAXS was used to examine the morphology at the end of each process. The lamellar morphology was generally preserved, except for samples within the shaded region.
Figure 5.6 SAXS of as-made film and after subsequent etching by 8 M TFA vapor at 40°C for 32 hr (a). The samples were indexed for LAM symmetry with peaks indicated at q/q*=1, 2, 3, and 4 where q=4πsin(θ)/λ. The lines in (a) were offset vertically for clarity. (b) top-view SEM images of mesoporous PS monolith resulting from TFA-vapor-etch.

5.5 Conclusion

In summary, TFA was found to be an ideal etchant for PLA removal from thick block copolymer films. The high etch rate of up to 14 nms⁻¹ enabled the complete removal of PLA from 2 mm thick films in less than 1 day. The use of a short etch process decreases the extent of PS damage to be below the detection limit. Etching with optimized TFA solutions also demonstrated preservation of the parent morphology as determined by SAXS and SEM. A combination of GPC and NMR confirmed that the only product was pristine porous PS with a molar mass distribution indistinguishable from the starting macrointiator. The combination of ¹H-NMR, HSQC, and GPC indicate that the TFA etch process did not induce detectable damage to the PS block, despite replacing the adjacent initiator group.
with a COOH. We anticipate that this significantly improved TFA etch process will impact numerous nanomaterial developments based upon access to porous polymers.

5.6 References


38. Scherer, M. PhD Thesis, University of Cambridge, **2012**.


CHAPTER 6

SUMMARY AND SUGGESTION FOR FUTURE WORK
6.1 Summary

We have improved few aspects of nanoscale porous material fabrication employing block copolymer self-assembly. One of the major objectives of this dissertation was to explore the right condition for achieving independent architecture control in porous material. A highly reproducible kinetic entrapment pathway was developed in order to ensure getting materials with constant ~13 nm pores with tunable 6-9 nm wall-dimensions with atomic level precision. To this end, a facile synthetic approach was developed in order to supply large quantities of structure directing agent PEO-b-PHA. Perhaps, the most intriguing result of this study is the introduction of versatile one-pot titration approach and a SAXS based geometric model that expedite PMT fabrication.

Prior work demonstrated PMT kinetics regulation using cosolvent amount that causes some deleterious effects up on excess addition, for e.g.; secondary pore formation in the material wall. An improved pathway was presented in the second part, that shows better control on polymer kinetics via solution thermodynamics where the major solvent maintains high energy barrier and small cosolvent amount preserves persistency. This approach demonstrates a framework to achieve PMT with smaller feature sizes (≤10 nm).

PMT for a range of various pore dimension is significantly inhibited by requirement of different molar masses polymers that demand heavy synthetic effort. To overcome this challenge, a pore swelling approach under kinetic control was developed which leads to the use of fewer polymers and cover a wide range of length scales of both pore size and wall-thickness tunability. This was demonstrated further successfully by tuning pore sizes in the range of 15-25 nm from a single polymer.
Lastly, focus was turned to the other direction where mesoporous organic templates were fabricated from lactide containing block copolymer self-assembled structure followed by selective degradation of polylactide moiety using our newly designed trifluoroacetic acid etching method. This etching technique was proved to be an ideal etchant for polylactide as nanostructure retained after complete removal. Additionally, the etching is quite fast and selective, especially for ~2 mm thick film, compared to the popular alkaline sodium hydroxide etching. In conclusion, this dissertation collectively discusses few improved aspects of porous nanostructured material fabrication.

6.2 Suggestion for Future Work

PMT is an area that would be better, and much future work should focus on the uses with possibilities for commercialization. As future direction, it can be envisioned PMT as a very powerful tool in several energy conversion and storage devices as it offers independent control on architectural dimension. Present study concentrates on a single material, niobium oxide. In future work, we will seek to investigate PMT in different materials system, for e.g., mesoporous carbons, tin oxide, and titania, as they are potential candidates for application in adsorption, separation, catalysis, photoelectrochemical water splitting devices, fuel cell, electrochromic devices, batteries and supercapacitors.\(^1\)\(^3\) Above discussed results are the exploratory study comparing a key, high $\chi$ block copolymer, PEO-b-PHA and a spherical micelle morphology. Fluorinated block copolymers are encouraging to investigate in PMT as they are expected to entrap micelles kinetically more efficiently compared to PEO-b-PHA. Further studies are required to explore PMT more closely on different morphologies, for e.g.; cylinder, vesicle, bicontinuous or different hierarchy structures for greater uses in energy device fabrication.
6.3 References


APPENDIX A

CHAPTER 2 SUPPORTING INFORMATION
Figure A.1 Photographs of each step of the PEO-\textit{b}-PHA synthesis, dissolution of PEO-OH (a) followed by the addition of DCC and DMAP (b), filtration (c), recovery of crude PEO-Br (d), purification of PEO-Br (e), sparging the polymerization solution (f), ATRP reaction (g-h), removal of copper salts (i-j), precipitation (k-l) and recovery of pure PEO-\textit{b}-PHA after solvent evaporation (m).

Figure A.2 Photographs of micelle templating steps, including sonication induced exchange of micelle solution (a), home-made spin coater with humidity control (b), application of solution to substrate (normally performed through a hole in the lid) (c), prompt sample aging (d). Some samples were calcined (e), for SEM imaging in cross-section (f), and top-view (g).
Table A.1 Change of PEO-\textit{b}-PHA micelles with sonication induced exchange as measured by DLS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Hydrodynamic Diameter (nm)</th>
<th>Standard deviation (nm)</th>
<th>Standard Deviation/Average (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As micellized</td>
<td>33.5</td>
<td>7.31</td>
<td>21.8%</td>
</tr>
<tr>
<td>Sonicated 5 min</td>
<td>21.4</td>
<td>3.12</td>
<td>14.6%</td>
</tr>
</tbody>
</table>

Table A.2 PEO-\textit{b}-PHA synthesis conditions.

<table>
<thead>
<tr>
<th>Trials</th>
<th>[M]:[I]:[Cu(I)]:[L]</th>
<th>Temp ((^\circ)C)</th>
<th>Reaction Time (h)</th>
<th>D(^a)</th>
<th>% monomer conversion(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100:1:0.25:0.25(^c)</td>
<td>70</td>
<td>15</td>
<td>1.36</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>100:1:0.50:0.50(^c)</td>
<td>70</td>
<td>10</td>
<td>1.11</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>100:1:0.50:0.50(^c)</td>
<td>80</td>
<td>15</td>
<td>1.10</td>
<td>49</td>
</tr>
<tr>
<td>4</td>
<td>100:1:0.50:0.50(^c)</td>
<td>100</td>
<td>18</td>
<td>1.53</td>
<td>71</td>
</tr>
<tr>
<td>5</td>
<td>100:1:1:1(^c)</td>
<td>70</td>
<td>15</td>
<td>1.89</td>
<td>87</td>
</tr>
<tr>
<td>6</td>
<td>100:1:1:1(^d)</td>
<td>70</td>
<td>15</td>
<td>1.13</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>100:1:1:1(^d)</td>
<td>70</td>
<td>24</td>
<td>1.15</td>
<td>50</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Trials</th>
<th>[M]:[I]:[Cu(I)]:[L]</th>
<th>Temp ((^\circ)C)</th>
<th>Reaction Time (h)</th>
<th>D(^a)</th>
<th>% monomer conversion(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100:1:0.25:0.25(^c)</td>
<td>70</td>
<td>15</td>
<td>1.36</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>100:1:0.50:0.50(^c)</td>
<td>70</td>
<td>10</td>
<td>1.11</td>
<td>28</td>
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<tr>
<td>3</td>
<td>100:1:0.50:0.50(^c)</td>
<td>80</td>
<td>15</td>
<td>1.10</td>
<td>49</td>
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<tr>
<td>4</td>
<td>100:1:0.50:0.50(^c)</td>
<td>100</td>
<td>18</td>
<td>1.53</td>
<td>71</td>
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<tr>
<td>5</td>
<td>100:1:1:1(^c)</td>
<td>70</td>
<td>15</td>
<td>1.89</td>
<td>87</td>
</tr>
<tr>
<td>6</td>
<td>100:1:1:1(^d)</td>
<td>70</td>
<td>15</td>
<td>1.13</td>
<td>20</td>
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<tr>
<td>7</td>
<td>100:1:1:1(^d)</td>
<td>70</td>
<td>24</td>
<td>1.15</td>
<td>50</td>
</tr>
</tbody>
</table>

\(^a\)obtained from GPC analysis, \(^b\)calculated using \(^1\)H NMR, \(^c\)Me6TREN and \(^d\)HMTETA were used as ligands.
Figure A.3 Cross-sectional SEM image of micelle template sample from series W7.5 where the nominal film thickness was 570 nm.

Figure A.4 Azimuthally integrated SAXS data from sample W7.5-1.21 before and after calcination. The dashed line indicates that the primary peak position was preserved, suggesting preservation of the in-plane lattice constant.
Figure A.5 GIWAXS of sample W7.5-1.21 after calcination to 500°C demonstrating crystalline Nb$_2$O$_5$ consistent with PDF#27-1003. The 2D image was inset where the color scale corresponds to the log of X-ray intensity.

**Derivation of SAXS based Geometric Models**

Calculations based on SAXS measurements provide the fundamental micelle-to-micelle spacing. First, we will start with simple cubic structures and consider two configurations of the micelles relative to the material. Then we will show an extension to a general case. The general case uses a simple correlation of SAXS and real-space measurements to enable modeling without identification of the specific space group. This extension to generic primitive lattices accommodates paracrystalline arrangements containing disorder.

The sample preparation conditions define an anticipated volume fraction for each component based upon the amount of material added relative to the amount of template. The use of density terms allows conversion of these volume fractions to the internal morphology separation of template and material. Thus knowledge of the micelle-to-micelle spacing enables deconvolution of template and material dimensions based on a density term and the material:template (M:T) ratio. Two models are considered, differing based upon the interaction of the corona block with the material being templated.

**Whole Micelle Template (WMT) Model:**

Consider a simple cubic (SC), body-centered cubic (BCC), or face-centered cubic (FCC) lattice:
The WMT model assumes that the material being templated is excluded from the entire volume of the micelle (manuscript **Scheme 1** top). Thus the template volume \( V_{\text{template}} \) per unit cell is a function of the sphere radius, \( r \), and the number of spheres per unit cell, \( n \):

\[
V_{\text{template}} = \frac{4n\pi r^3}{3} \quad \text{(eq 1)}
\]

Here, \( n = 1 \) for a simple cubic lattice, \( n = 2 \) for a body-centered cubic lattice, and \( n = 3 \) for a face-centered cubic lattice.

The matrix volume is occupied solely by the material being templated. Since the total volume of the unit cell is \( a^3 \), the volume of matrix per unit cell is:

\[
V_{\text{material}} = a^3 - \frac{4n\pi r^3}{3} \quad \text{(eq 2)}
\]

where the lattice constant is \( a \). The material:template mass ratio (\( M:T=x \)) is used as a convenient handle to quantify titration of material into a micelle template solution. The definition of \( x \) is thus:

\[
x \equiv \frac{m_{\text{material}}}{m_{\text{template}}} = \frac{V_{\text{material}} \rho_{\text{material}}}{V_{\text{template}} \rho_{\text{template}}} \quad \text{(eq 3)}
\]

where \( \rho \) terms correspond to component densities. Combining equations (1) and (2) into (3) yields:

\[
x = \frac{\rho_{\text{material}} \left( a^3 - \frac{4n\pi r^3}{3} \right)}{\frac{4n\pi r^3}{3} - \rho_{\text{template}}} \quad \text{(eq 4)}
\]

This equation may be reorganized after solving for template sphere radius, \( r \), to yield:

\[
r = a \sqrt[3]{\frac{3}{4\pi \left(1 + \frac{x \rho_{\text{template}}}{\rho_{\text{material}}}\right)}} \quad \text{(eq 5)}
\]

The density terms are combined for fitting a single convolved density term \( \beta \) defined as:
The template or pore radius may thus be predicted based upon a lattice measurement by SAXS (a), the M:T ratio (x), and a single fit parameter for relative densities, $\beta$:

$$r = a \sqrt[3]{\frac{3}{4n\pi (1 + x\beta_{\text{wmt}})}}$$  \hspace{1cm} (eq 7)

The micelle or pore diameter, D, is found simply by multiplying this radius by 2. This cubic form of the WMT model will later be extended to non-cubic or disordered systems by accounting for the specific relationship of micelle-to-micelle spacing to the observed by SAXS peak.

**Micelle Core Template (MCT) Model:**

The MCT model assumes that the material being templated is excluded from the core of the micelle (manuscript *Scheme 1* bottom). Thus the template volume per unit cell ($V_{\text{template}}$) is a function of the sphere radius, r, and the number of spheres per unit cell, n:

$$V_{\text{template}} = V_{\text{core}} = \frac{4n\pi r^3}{3}$$  \hspace{1cm} (eq 8)

Here we address a few cubic lattices where $n = 1$ for a simple cubic, $n = 2$ for a body-centered cubic, and $n = 3$ for a face-centered cubic. The matrix volume is occupied by a combination of the material being template and the corona chains, in this case PEO. Since the total volume of the unit cell is $a^3$, the volume of matrix per unit cell is:

$$V_{\text{matrix}} = a^3 - \frac{4n\pi r^3}{3} = V_{\text{material}} + V_{\text{corona}}$$  \hspace{1cm} (eq 9)

Again, the material:template mass ratio (M:T=x) is used as a convenient handle to quantify the titration of materials into a micelle template solution. Please note that for experimental convenience, we define the template mass as the total polymer mass, including both core are corona. The definition of x is the same as before, however the expression of x in terms of material volumes and densities changes somewhat:

$$x = \frac{V_{\text{material}}\rho_{\text{material}}}{V_{\text{core}}\rho_{\text{core}} + V_{\text{corona}}\rho_{\text{corona}}}$$  \hspace{1cm} (eq 10)

where volume terms V are for each component per unit cell and density terms are for each component. The corona volume per unit cell may be found based on the volume fractions of the block copolymer where:

$$V_{\text{corona}} = V_{\text{template}} \frac{f_{\text{corona}}}{1 - f_{\text{corona}}}$$  \hspace{1cm} (eq 11)
In this manuscript, PEO is the corona block and PHA is the core/template block. Substituting equation 8, 9, and 11 into equation 10 yields an equation that may be simplified to:

\[ x = \frac{\rho_{\text{material}}}{\rho_{\text{core}} + f_{\text{corona}} \rho_{\text{corona}}} \left( \frac{3a^3}{4n\pi} - 1 - \frac{f_{\text{corona}}}{1 - f_{\text{corona}}} \right) \]  
(eq 12)

Solving (12) for radius yields the following expression:

\[ r = a \sqrt[3]{\frac{3}{4n\pi}} \left( \frac{x}{\frac{\rho_{\text{material}}}{\rho_{\text{core}} + f_{\text{corona}} \rho_{\text{corona}}}} + 1 + \frac{f_{\text{corona}}}{1 - f_{\text{corona}}} \right)^{-1/3} \]  
(eq 13)

that may be simplified by defining a relative density parameter as:

\[ \beta_{\text{mct}} \equiv \frac{\rho_{\text{core}} + f_{\text{corona}} \rho_{\text{corona}}}{\rho_{\text{material}}} \]  
(eq 14)

Substituting (14) into (15) yields the simplified expression:

\[ r = a \sqrt[3]{\frac{3}{4n\pi}} \left( x \beta_{\text{mct}} + 1 + \frac{f_{\text{corona}}}{1 - f_{\text{corona}}} \right)^{-1/3} \]  
(15)

Again, the template or pore diameter, D, is found simply by multiplying this radius by 2. This cubic form of the MCT model will next be extended to non-cubic or paracrystalline systems.

**Triclinic and Paracrystalline Systems**

Consider a primitive cell that is equilateral and triclinic:
This parallelepiped imposes a geometric constraint similar to the cubic cases above based upon the relative volume fractions of each component. For the non-cubic MCT case, equation 8 remains unchanged with n=1. However, the unit cell volume scales with the micelle-to-micelle spacing as:

\[ V_{\text{unit cell}} = \gamma d_{m-m}^3 \quad (16) \]

where \( \gamma \) is a scalar less than or equal to 1.0 and \( d_{m-m} \) is the micelle-to-micelle spacing. The \( d_{m-m} \) may be found from SAXS measurements after establishing a correlation with real-space data, using a scalar conversion, \( S \):

\[ S = \frac{d_{m-m}}{d_{\text{spacing}}} = \frac{qd_{m-m}}{2\pi} \quad (17) \]

where \( q \) is an easily tracked structure factor feature such as a maximum or minimum in SAXS. Here we used the first SAXS maxima for the presented data in the manuscript. The MCT matrix volume may then be expressed as:

\[ V_{\text{matrix}} = V_{\text{material}} + V_{\text{corona}} = \gamma d_{m-m}^3 - \frac{4\pi r^3}{3} \quad (18) \]

Substituting equations 8, 11, and 18 into equation 10 may be simplified to yield:

\[ x = \frac{\rho_{\text{material}}}{\rho_{\text{core}} + \frac{f_{\text{corona}}}{1-f_{\text{corona}}} \rho_{\text{corona}}} \left( \frac{3\gamma d_{m-m}^3}{4\pi r^3} - 1 - \frac{f_{\text{corona}}}{1-f_{\text{corona}}} \right) \quad (19) \]

This may be solved for radius, yielding:

\[ r = d_{m-m} \left( \frac{3\gamma}{4\pi} \left( x\beta_{\text{mct}} + 1 + \frac{f_{\text{corona}}}{1-f_{\text{corona}}} \right) \right)^{-1/3} \quad (20) \]

Again, the template or pore diameter, \( D \), is found simply by multiplying this radius by 2. This generic form of the MCT model may be used to extract pore dimensions from SAXS data using directly measured values (\( S \) and \( f \)) and two fit parameters (\( \gamma \) and \( \beta \)). Please note the similarity to equation 15, the MCT model for cubic systems. In the context of micelle templates, we expect typical \( \gamma \) values to be \( \sim 1 \), with limited distortion.

A similar derivation for the non-cubic WMT model yields a result closely related to equation 7:

\[ r = d_{m-m} \left( \frac{3\gamma}{4\pi \left( 1 + x\beta_{\text{wmt}} \right)} \right)^{3/2} \quad (21) \]
The Material Wall-Thickness Derivation

The WMT and MCT models provide the template/pore dimensions. The material wall-thickness is a natural outcome from identifying component geometries, independent of which model was used. One added complexity is that material wall-thickness varies with crystallographic direction. For example, the wall-thicknesses in major directions of a BCC lattice are:

\[ w_{100} = a - D \]
\[ w_{110} = \sqrt{2}a - D \]
\[ w_{111} = \frac{\sqrt{3}}{2}a - D \] (eq 22-24)

Considering the convoluted distribution wall-thicknesses, we propose an expression for the nominal wall-thickness using an additional fit term, \( \alpha \) to accommodate the variable distribution of wall-thickness contributions for any candidate lattice:

\[ w = (\alpha a - D) \] (eq 25)

For cubic crystal systems, we anticipate that alpha values \( \sim 1 \pm 0.5 \) to be typical.

Figure A.6 WAXS of sample W7.5-1.21 (a,b) and PEO crystals (a,c). The lack of PEO crystallites in templated films suggests that the PEO corona are mixed with the material. DSC data of W7.5-1.21 also lacked any observable PEO crystallization, also suggesting PEO corona mixing with the material being template (d-e).
Figure A.7 1D SAXS plot of micelle template samples prepared under different relative humidity conditions.

Figure A.8 Map of SAXS d-spacing uniformity across a 6x6 mm² area of a sample W-7.5-1.19. The X and Y axis correspond to sample position and the d-spacing was calculated was the best-fit of the first SAXS peak. A total of 25 measurements were taken. The average d-spacing was 21.95 nm with a standard deviation of 0.145 nm, corresponding to <1% variation.
Figure A.9 Best fit results for the combined 3 trial runs of sample series W7.5 using the WMT model for d-spacing (a), pore diameter (b), and wall-thickness (c). PMT titration curves are shown as dotted lines and feature sizes were separately calculated based on each SAXS pattern as compared to SEM data.

Table A.3 Calculations resulting from the best fit evaluation of the WMT model with sample series W7.5.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>PMT Titration Curve (WMT model)</th>
<th>WMT Interpretation of SAXS Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d-spacing (nm)</td>
<td>Wall-Thickness (nm)</td>
</tr>
<tr>
<td>W7.5-1.13</td>
<td>21.46</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-1.21</td>
<td>21.88</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-1.39</td>
<td>22.78</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-1.46</td>
<td>23.11</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-1.58</td>
<td>23.65</td>
<td>12.74</td>
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<td>W7.5-1.77</td>
<td>24.46</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-1.94</td>
<td>25.14</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-2.07</td>
<td>25.64</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-2.24</td>
<td>26.27</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-2.30</td>
<td>26.50</td>
<td>12.74</td>
</tr>
<tr>
<td>W7.5-2.42</td>
<td>26.90</td>
<td>12.74</td>
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<tr>
<td>W7.5-2.47</td>
<td>27.07</td>
<td>12.74</td>
</tr>
</tbody>
</table>
Table A.4 Best fit parameters for the WMT model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>0.99(^a)</td>
</tr>
<tr>
<td>( \beta ) density</td>
<td>4.9316(^a)</td>
</tr>
<tr>
<td>PEO volume fraction</td>
<td>38%(^b)</td>
</tr>
<tr>
<td>( S )</td>
<td>0.8963(^c)</td>
</tr>
<tr>
<td>( \Upsilon )</td>
<td>1.00(^a)</td>
</tr>
<tr>
<td>( \delta ) Pore size (nm)</td>
<td>12.74(^d)</td>
</tr>
</tbody>
</table>

\(^a\) determined by least squares fitting within PMT window  
\(^b\) determined by NMR analysis of polymer  
\(^c\) average S value for all samples within PMT window determine by SEM and SAXS  
\(^d\) average pore data for all samples within PMT window.

Table A.5 MCT model calculations for series W7.5 based upon fit values established from a limited dataset that included SEM measurements from a single sample W7.5-1.13 and all SAXS data.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>PMT Titration Curve (MCT Model)</th>
<th>MCT Interpretation of SAXS Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d-spacing (nm)</td>
<td>Pore Size (nm)</td>
</tr>
<tr>
<td>W7.5-1.13</td>
<td>21.63</td>
<td>12.43</td>
</tr>
<tr>
<td>W7.5-1.21</td>
<td>22.01</td>
<td>12.43</td>
</tr>
<tr>
<td>W7.5-1.39</td>
<td>22.83</td>
<td>12.43</td>
</tr>
<tr>
<td>W7.5-1.46</td>
<td>23.13</td>
<td>12.43</td>
</tr>
<tr>
<td>W7.5-1.58</td>
<td>23.63</td>
<td>12.43</td>
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<tr>
<td>W7.5-1.77</td>
<td>24.38</td>
<td>12.43</td>
</tr>
<tr>
<td>W7.5-1.94</td>
<td>25.02</td>
<td>12.43</td>
</tr>
<tr>
<td>W7.5-2.07</td>
<td>25.48</td>
<td>12.43</td>
</tr>
<tr>
<td>W7.5-2.24</td>
<td>26.06</td>
<td>12.43</td>
</tr>
<tr>
<td>W7.5-2.30</td>
<td>26.28</td>
<td>12.43</td>
</tr>
<tr>
<td>W7.5-2.42</td>
<td>26.65</td>
<td>12.43</td>
</tr>
<tr>
<td>W7.5-2.47</td>
<td>26.81</td>
<td>12.43</td>
</tr>
</tbody>
</table>

Table A.6 Fit parameters for series W7.5 established from a limited dataset that included SEM measurements from a single sample W7.5-1.13 and all SAXS data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>1.09(^b)</td>
</tr>
<tr>
<td>( \beta ) density</td>
<td>3.6281(^a)</td>
</tr>
<tr>
<td>PEO volume fraction</td>
<td>38%(^b)</td>
</tr>
<tr>
<td>( S )</td>
<td>0.8113(^c)</td>
</tr>
<tr>
<td>( \Upsilon )</td>
<td>1.00(^b)</td>
</tr>
</tbody>
</table>

\(^a\) determined by least squares fitting within PMT window  
\(^b\) determined by NMR analysis of polymer  
\(^c\) S value for samples W7.5-1.13 determined by SEM and SAXS  
\(^d\) average of pore size of sample W7.5-1.1
APPENDIX B

CHAPTER 3 SUPPORTING INFORMATION
Figure B.1 SEM of film made using PEO-\textit{b}-PHA diblock copolymer (12.7 kgmol\textsuperscript{-1}, D = 1.10) with 17\% water and M:T=1.50. The primary pores (12.50±0.218 nm) are accompanied by secondary porosity indicated with arrows (4.57±0.133 nm).

Figure B.2 \textsuperscript{1}H NMR (a), and GPC (b) of OH diblock copolymer demonstrating controlled chain extension with narrow molar mass dispersity.
Derivation of Log-Log Coordinate Space for Validation of SAXS Consistency with PMT Lattice Expansion:

A relationship was previously derived\(^{26}\) to predict micelle template or pore size based upon SAXS measurements using a simple lattice model and a conservation of volume argument. There the micelle template radius \(r\) scaled with:

\[
r = Cd^* \left( x \beta_{mct} + 1 + \frac{f_{\text{corona}}}{1 - f_{\text{corona}}} \right)^{-1/3}
\]  

(eq S1)

where the constant \(C\) had specific values depending on symmetry, or lack thereof in the paracrystalline case. Here \(d^*\) is the \(d\)-spacing corresponding to the first SAXS structure factor peak, \(x\) is the material:template ratio, and \(f_{\text{corona}}\) is the volume fraction of the corona block. Rearranging (eq S1) to solve for \(d^*\) results in:

\[
d^* = \frac{r}{C} \left( x \beta_{mct} + 1 + \frac{f_{\text{corona}}}{1 - f_{\text{corona}}} \right)^{1/3}
\]  

(eq S2)

Taking the log of both sides and simplifying results in:

\[
\log(d^*) = \log\left(\frac{r}{C}\right) + \frac{1}{3} \log \left( x \beta_{mct} + 1 + \frac{f_{\text{corona}}}{1 - f_{\text{corona}}} \right)
\]  

(eq S3)

The resulting equation provides a simple linear relationship on a log-log plot of \(d^*\) vs a term with \(x\). However, the \(\beta_{mct}\) in this term is an experimental fit parameter that is rarely known apriori. Since \(3>x>1\), \(\beta_{mct}>\sim 4\) and \(f_{\text{corona}}<0.4\) so one may approximate that:

\[
x \beta_{mct} + 1 + \frac{f_{\text{corona}}}{1 - f_{\text{corona}}} \approx x \beta_{mct}
\]  

(eq S4)

This approximation allows (eq S3) to be approximated as:
Here the kinetic entrapment of persistent micelle conditions would maintain constant radius \( r \) where the lattice expansion of \( d^* \) is a result of increasing the wall-thickness alone. Under these conditions a log-log plot of \( d^* \) vs \( x \) should be approximately a straight line with slope of 1/3. This relationship provides considerable utility for fitting where the fit region may be constrained based upon intrinsic scaling relationships for \( d^* \) to \( x \) based on this simple scaling relationship.

\[
\log(d^*) \approx \log\left(\frac{r}{C}\right) + \frac{1}{3} \log(x) = \log\left(\frac{r}{C}\right) + \frac{1}{3} \log(\beta_{mct}) + \frac{1}{3} \log(x) \quad (eq \ S5)
\]

Figure B.3 SAXS measurements of OH-THF-Series1 with increasing Material:Template ratio. The scattering data were offset vertically for clarity.

Figure B.4 SEM images of OH-THF-Series1 after calcination. The Material:Template ratios are 1.26 (a), 1.34 (b), 1.40 (c), 1.46 (d), 1.53 (e), 1.63 (f) and 1.92 (g).
Table B.1 Measurements of OH-THF-Series

<table>
<thead>
<tr>
<th>Sample</th>
<th>M:T ratio</th>
<th>SAXS d-spacing (nm)</th>
<th>SEM average pore diameter (nm)</th>
<th>SEM average wall thickness (nm)</th>
<th>Wall:Pore ratio (unitless)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH-THF-series1-1.26</td>
<td>1.26</td>
<td>20.91±1.40</td>
<td>12.88±0.191</td>
<td>6.02±0.194</td>
<td>0.47</td>
</tr>
<tr>
<td>OH-THF-series1-1.34</td>
<td>1.34</td>
<td>21.12±0.34</td>
<td>12.16±0.119</td>
<td>6.29±0.169</td>
<td>0.52</td>
</tr>
<tr>
<td>OH-THF-series1-1.40</td>
<td>1.40</td>
<td>21.39±0.81</td>
<td>12.65±0.197</td>
<td>6.61±0.294</td>
<td>0.52</td>
</tr>
<tr>
<td>OH-THF-series1-1.46</td>
<td>1.46</td>
<td>21.42±0.23</td>
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<td>6.60±0.308</td>
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<tr>
<td>OH-THF-series1-1.53</td>
<td>1.53</td>
<td>22.45±0.68</td>
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<tr>
<td>OH-THF-series1-1.64</td>
<td>1.63</td>
<td>23.82±1.52</td>
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<td>7.58±0.247</td>
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<td>OH-THF-series1-1.72</td>
<td>1.72</td>
<td>24.50±1.94</td>
<td>11.87±0.209</td>
<td>9.59±0.208</td>
<td>0.81</td>
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<tr>
<td>OH-THF-series1-1.83</td>
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<td>24.86±1.21</td>
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<tr>
<td>OH-THF-series1-1.92</td>
<td>1.92</td>
<td>25.51±0.62</td>
<td>12.13±0.193</td>
<td>8.18±0.329</td>
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</tr>
<tr>
<td>OH-THF-series1-2.05</td>
<td>2.05</td>
<td>25.90±0.97</td>
<td>11.57±0.21</td>
<td>9.14±0.369</td>
<td>0.79</td>
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<tr>
<td>OH-THF-series2-1.26</td>
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<td>OH-THF-series2-1.40</td>
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<tr>
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<tr>
<td>OH-THF-series2-1.72</td>
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<td>25.11</td>
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<tr>
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<td>20.15</td>
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<td>20.48</td>
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<td>20.78</td>
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<td>21.12</td>
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<tr>
<td>OH-THF-series3-1.60</td>
<td>1.60</td>
<td>20.34</td>
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<tr>
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<td>1.64</td>
<td>20.59</td>
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<td>--</td>
<td>--</td>
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<tr>
<td>OH-THF-series3-1.77</td>
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<td>22.27</td>
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<td>1.87</td>
<td>24.25</td>
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<tr>
<td>OH-THF-series3-1.95</td>
<td>1.95</td>
<td>29.51</td>
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<td>--</td>
</tr>
<tr>
<td>OH-THF-series3-2.01</td>
<td>2.01</td>
<td>23.16</td>
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</tr>
</tbody>
</table>

Figure B.5 SEM images of OH-EtOH-Series1 in order of increasing Material:Template ratio: 1.29 (a), 1.36 (b), 1.44 (c), 1.53 (d), 1.64 (e), 1.71 (f) 1.85 (g), 1.97 (h), 2.06 (i), 2.29 (j), 2.39 (k), and 2.51 (l).
Figure B.6  SAXS of OH-EtOH-Series1 with the increasing Material:Template ratio. The scattering data were offset vertically for clarity.

Table B.2 Measurements of OH-EtOH-Series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>M:T ratio</th>
<th>SAXS d-spacing (nm)</th>
<th>SEM average pore diameter (nm)</th>
<th>SEM average wall-thickness (nm)</th>
<th>Wall:Poore ratio (unitless)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH-EtOH-series1-1.29</td>
<td>1.29</td>
<td>19.85±0.174</td>
<td>11.97±0.207</td>
<td>5.86±0.248</td>
<td>0.49</td>
</tr>
<tr>
<td>OH-EtOH-series1-1.36</td>
<td>1.36</td>
<td>19.74±0.161</td>
<td>11.64±0.107</td>
<td>7.04±0.185</td>
<td>0.60</td>
</tr>
<tr>
<td>OH-EtOH-series1-1.44</td>
<td>1.44</td>
<td>20.01±0.078</td>
<td>11.79±0.156</td>
<td>6.08±0.194</td>
<td>0.52</td>
</tr>
<tr>
<td>OH-EtOH-series1-1.53</td>
<td>1.53</td>
<td>20.42±0.141</td>
<td>11.75±0.156</td>
<td>6.58±0.159</td>
<td>0.56</td>
</tr>
<tr>
<td>OH-EtOH-series1-1.58</td>
<td>1.58</td>
<td>20.61±0.198</td>
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</tr>
<tr>
<td>OH-EtOH-series1-1.64</td>
<td>1.64</td>
<td>21.03±0.27</td>
<td>11.71±0.164</td>
<td>6.74±0.153</td>
<td>0.58</td>
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<tr>
<td>OH-EtOH-series1-1.71</td>
<td>1.71</td>
<td>21.31±0.18</td>
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<td>6.81±0.188</td>
<td>0.57</td>
</tr>
<tr>
<td>OH-EtOH-series1-1.85</td>
<td>1.85</td>
<td>21.69±0.149</td>
<td>12.03±0.184</td>
<td>7.18±0.177</td>
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<tr>
<td>OH-EtOH-series1-1.97</td>
<td>1.97</td>
<td>22.67±0.103</td>
<td>12.00±0.232</td>
<td>7.10±0.270</td>
<td>0.59</td>
</tr>
<tr>
<td>OH-EtOH-series1-2.06</td>
<td>2.06</td>
<td>23.13±0.171</td>
<td>10.43±0.175</td>
<td>5.83±0.255</td>
<td>0.56</td>
</tr>
<tr>
<td>OH-EtOH-series1-2.29</td>
<td>2.29</td>
<td>24.29±0.344</td>
<td>12.14±0.168</td>
<td>7.23±0.253</td>
<td>0.60</td>
</tr>
<tr>
<td>OH-EtOH-series1-2.39</td>
<td>2.39</td>
<td>25.19±0.156</td>
<td>11.45±0.162</td>
<td>8.16±0.267</td>
<td>0.71</td>
</tr>
<tr>
<td>OH-EtOH-series1-2.51</td>
<td>2.51</td>
<td>28.20±0.352</td>
<td>12.23±0.185</td>
<td>8.28±0.346</td>
<td>0.68</td>
</tr>
<tr>
<td>OH-EtOH-series2-1.52</td>
<td>1.52</td>
<td>20.42</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>OH-EtOH-series2-1.64</td>
<td>1.64</td>
<td>20.94</td>
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<td>--</td>
</tr>
<tr>
<td>OH-EtOH-series2-1.75</td>
<td>1.75</td>
<td>21.70</td>
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</tr>
<tr>
<td>OH-EtOH-series2-1.95</td>
<td>1.95</td>
<td>21.94</td>
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<td>--</td>
<td>--</td>
</tr>
<tr>
<td>OH-EtOH-series2-2.05</td>
<td>2.05</td>
<td>22.52</td>
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</tr>
<tr>
<td>OH-EtOH-series2-2.11</td>
<td>2.11</td>
<td>22.77</td>
<td>11.41±0.187</td>
<td>6.06±0.282</td>
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<tr>
<td>OH-EtOH-series2-2.25</td>
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<td>22.59</td>
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</tr>
<tr>
<td>OH-EtOH-series2-2.37</td>
<td>2.37</td>
<td>23.69</td>
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<td>--</td>
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</tr>
<tr>
<td>OH-EtOH-series2-2.46</td>
<td>2.46</td>
<td>25.00</td>
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</tr>
</tbody>
</table>
Figure B.7 SAXS of OH-MeOH-Series1 with increasing Material:Template ratio. The scattering data were offset vertically for clarity.

Table B.3 Measurements of OH-MeOH-Series samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>M:T ratio</th>
<th>SAXS d-spacing (nm)</th>
<th>SEM average pore diameter (nm)</th>
<th>SEM average wall-thickness (nm)</th>
<th>Wall:Pore ratio (unitless)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH-MeOH-series1-1.09</td>
<td>1.09</td>
<td>20.74±0.11</td>
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<td>--</td>
<td>--</td>
</tr>
<tr>
<td>OH-MeOH-series1-1.23</td>
<td>1.23</td>
<td>21.09±0.23</td>
<td>12.75±0.174</td>
<td>6.24±0.194</td>
<td>0.49</td>
</tr>
<tr>
<td>OH-MeOH-series1-1.31</td>
<td>1.31</td>
<td>21.44±0.11</td>
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<td>--</td>
</tr>
<tr>
<td>OH-MeOH-series1-1.37</td>
<td>1.37</td>
<td>21.67±0.13</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>OH-MeOH-series1-1.50</td>
<td>1.50</td>
<td>22.14±0.13</td>
<td>12.95±0.234</td>
<td>7.44±0.213</td>
<td>0.57</td>
</tr>
<tr>
<td>OH-MeOH-series1-1.60</td>
<td>1.60</td>
<td>22.72±0.30</td>
<td>13.02±0.178</td>
<td>7.80±0.312</td>
<td>0.60</td>
</tr>
<tr>
<td>OH-MeOH-series1-1.68</td>
<td>1.68</td>
<td>23.05±0.12</td>
<td>13.29±0.170</td>
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<td>36.90</td>
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</table>
APPENDIX C

CHAPTER 4 SUPPORTING INFORMATION
Figure C.1 $^1$H NMR of OH$_1$ diblock copolymer demonstrating controlled chain extension with 14,737 g mol$^{-1}$.

Figure C.2 $^1$H NMR of h-PHA homopolymer with the Mn = 1,173 g mol$^{-1}$. 
Figure C.3 GPC of (a) PEO-Br macroinitiator with dispersity (\(\mathcal{D}\)) of 1.04 and (b) OH_1 diblock copolymer with dispersity (\(\mathcal{D}\)) of 1.11.

Figure C.4 GPC of h-PHA diblock copolymer with narrow molar mass dispersity of 1.36.

Table C.1 Characteristics of OH polymer used.

<table>
<thead>
<tr>
<th>h-PHA</th>
<th>(M_n) (gmol(^{-1})) (^a)</th>
<th>(\mathcal{D}) (^b)</th>
<th>Times (x) lighter than PHA in PEO-(b)-PHA</th>
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<tr>
<td>h-PHA</td>
<td>1.173</td>
<td>1.09</td>
<td>12.5x</td>
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<td>h-PHA-1</td>
<td>5.015</td>
<td>1.11</td>
<td>2.9x</td>
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<td>h-PHA-2</td>
<td>9.987</td>
<td>1.10</td>
<td>1.5x</td>
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</table>

\(^a\) obtained from \(^1\)H NMR analysis, \(^b\) obtained from GPC analysis.
Figure C.5 SEM images of mesoporous templates prepared by OH_1-MeOH with excess addition of h-PHA, 250% (a) and 500% (b) where homopolymer aggregates and started to phase separate from micelle core, shown by black blobs.

Figure C.6 OH_1 and h-PHA solution mixture in methanol. The cloudier solution (a) leads to the formation of homopolymer aggregates that phase separates from micelle core whereas the clear solution (b) avoids that possibility.
Figure C.7 SEM image of mesoporous templates prepared by OH$_1$-MeOH with 500% concentrations of h-PHA.

Figure C.8 SAXS of 80% h-PHA swelled sample series with increasing Material:Template ratio. The scattering data were offset vertically for clarity.
Figure C.9 SEM of 80% h-PHA loaded OH_1 micelle template.
APPENDIX D

CHAPTER 5 SUPPORTING INFORMATION
Figure D.1 The as-made PS-\(b\)-PLA 2D SAXS pattern consisting of isotropic rings. Color scale corresponds to the log of the X-ray intensity.

Figure D.2 (a) SAXS of as-made (2 mm thick) as compared to NaOH-etch (2mm thick) PS-\(b\)-PLA film. The samples were indexed for LAM symmetry with peaks indicated at \(q/q^*=1, 2, 3, 4, \) and 5. The scattering data were offset vertically for clarity. (b) Top-view SEM image of sample NaOH-etch.
Figure D.3 Heteronuclear single quantum coherence spectroscopy of sample TFA-etch.

Figure D.4 Heteronuclear single quantum coherence spectroscopy of PS-OH macroinitiator.
Figure D.5 Heteronuclear single quantum coherence spectroscopy of sample NaOH-etch. New and unidentified carbons resulting from the etch are indicated by arrows.

Figure D.6 The as-made samples resulted from a combination of solvent casting (a) and vacuum oven annealing (b). Samples were etched by immersion in a TFA solution (c) placed in an oven (d). The etched films were rinsed with water (e) and immersed in methanol (f) before drying in a vacuum oven.
Figure D.7 TFA vapor etching was conducted with the as-made sample and etchant solution placed adjacent within a closed jar (a). The entire setup was placed within an oven (b). The etched film was rinsed with water (c) and immersed in methanol (d) before drying in vacuum oven.

Figure D.8 PLA etch kinetics using the vapor from an 8M TFA solution.

PS-\textit{b}-PLA2 Synthesis:

PS-\textit{b}-PLA2 was synthesized following a similar procedure as PS-\textit{b}-PLA. The PS-OH was synthesized using reagent ratio of [Styrene]:[Initiator]:[Me$_6$TREN]:[Cu(I)]:[Sn(II)] = 300:1:0.105:0.005:0.1. After 12 hrs of
polymerization the PS-OH of 13.9 kg/mol and dispersity of 1.22 was obtained. The PS-\(b\)-PLA of 27.8 kg/mol with a molar mass dispersity (\(D\)) of 1.23 was obtained after 15 minutes of polymerization using a reagent ratio of [PS-OH]:[Lactide]:[DBU]:[Thiourea]=1:150:1.34:1.34. Sample HEX-As-Made was made using the already described annealing procedures. Sample HEX-TFA-Etch was prepared using immersion in 1M TFA solution for 27 hrs, following the already described procedures.

Table D.1 PS-\(b\)-PLA2 Characterization:

<table>
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<tr>
<th>Sample</th>
<th>(M_n,_{PS}) (kg mol(^{-1})) (^{a})</th>
<th>(M_n,_{PLA}) (kg mol(^{-1})) (^{b})</th>
<th>Total (M_n) (kg mol(^{-1})) (^{c})</th>
<th>(D) (^{a})</th>
<th>(f_{PS}) (^{d})</th>
<th>(f_{PLA}) (^{d})</th>
<th>Morphology (^{e})</th>
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</thead>
<tbody>
<tr>
<td>PS-(b)-</td>
<td>13.9</td>
<td>13.9</td>
<td>27.8</td>
<td>1.23</td>
<td>0.54</td>
<td>0.46</td>
<td>HEX</td>
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<tr>
<td>PLA2</td>
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</tbody>
</table>

\(^{a}\)obtained from GPC analysis, \(^{b}\)obtained from \(^{1}\)H NMR analysis, \(^{c}\)obtained from \(a+b\)

\(^{d}\)volume fractions (\(f\)) calculated using densities\(^{21,36}\) at 110°C, PS= 1.02 g/cm\(^3\), PLA = 1.18 g/cm\(^3\) \(^{e}\)Morphology determined by SAXS.
Figure D.9 (a) $^1$H NMR spectra of (i) HEX-As-Made and (ii) HEX-TFA-etch dissolved in CDCl$_3$. 100% of PLA was removed selectively (PLA peak disappeared at 5.19 ppm) by immersion in 1M TFA solution for 26 hrs. (b) SAXS of HEX-As-Made and HEX-TFA-etch demonstrate preservation of a hexagonal morphology. The principal peak ($q^*$) in both scattering profile is centered at 0.25 nm$^{-1}$. The samples were indexed for HEX symmetry with peaks indicated at $q/q^*$=1, $\sqrt{3}$, and $\sqrt{4}$. The scattering data were offset vertically for clarity. (c-d) Top-view SEM images of sample HEX-TFA-etch with a measured pore size of 16.2 ±2.5 nm.
Figure D.10 $^1$H NMR spectrum of bis (3.5-trifluoromethyl)-phenylcyclohexylthiourea co-catalyst.
APPENDIX E

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How to make persistent micelle templates in 24 hours and know it using X-ray scattering

DOI: 10.1039/C7TA01034F

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A. Sarkar and M. Stefkik, Mater. Chem. Front., 2017, 1, 1526

DOI: 10.1039/C6QM00266H

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