Block copolymer synthesis and self-assembly for membrane and lithographic applications

AN ABSTRACT SUBMITTED

ON THE 5TH DAY OF SEPTEMBER 2018

TO THE DEPARTMENT OF CHEMICAL AND BIOMOLECULAR
ENGINEERING IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
OF THE SCHOOL OF SCIENCE AND ENGINEERING OF
TULANE UNIVERSITY

FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

By

Baraka Shariff Lwoya

APPROVED:

Julie N. L. Albert, Ph.D.
Director
Vijay T. John, Ph.D.

Lawrence R. Pratt, Ph.D.

Wayne F. Reed, Ph.D.

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Abstract

Silicon-based block copolymers have gained prominence because of their inherent ability to self-assemble at the low molecular weight. By utilizing this vital factor, we synthesize poly(vinylmethysiloxane-block-methyl methacrylate) (PVMS-b-PMMA) intending to create small characteristic features with the potential application for lithography and membrane filtration. The polymer is made by a combination of anionic synthesis of PVMS, ATRP (atom radical transfer polymerization) of PMMA, and then co-joining the end-group functionalized blocks with a “click” reaction. After synthesis, thin films (10-100 nm) were self-assembled to form structures aligned perpendicular to the substrate. The morphology was observed by atomic force microscopy, grazing incidence small-angle X-ray scattering (GISAXS), and transmission electron microscopy (TEM). Additionally, the hydrophobicity of PVMS prompted us to develop a coating on microporous membrane supports for separation of water-in-oil mixtures. The PVMS was used as an effective coating to prevent fouling while maintaining high selectivity for both water-in-toluene and water-in-decane emulsion in gravity-based filtration. Finally, cyclic block copolymers (BCPs) have garnered increased attention because of their unique structure, which differs from linear BCPs due to a lack of end groups. This feature in combination with the high segregation strength of silicon-based polymers is desirable for nanolithography. Thus, we synthesized a new class of silicon-based cyclic polymer, cyclic PVMS-b-PMMA, intending to later understand the impact of topology on phase behavior, domain spacing, and nanoconfinement in thin films.
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Acknowledgments

The Ph.D. studies have been a long enduring process that was only made possible by the support of family, friends, and faculty at Tulane University.

I would first like to thank Dr. Julie Albert because without her this would have been impossible. I recall the first day I walked into her laboratory. She was very kind and meticulous in guiding me through the developmental process into a scientist. We have endured a long journey together and throughout the period, I have enjoyed learning polymer science.

In the course of Ph.D. studies, your support system certainly is important and will determine your success in the program. Through the years, I learned a lot from my friends George Ezeh and Antony Obanda. What started as three strangers living in a house together ended up in true kinship and brotherhood. Because of these two people, I maintained constant focus in my studies and obtained relief during challenging times by always enlisting their advice on both academic and personal matters.

To my lab member Sam Bleisner, Amy Goodson, Debaroty Roy and Saeed Behzadinasab it has truly been a pleasure working and learning from all of you. And to you Md. Fakar Uddin, you have become more than a lab-mate and I am proud to say that you are my brother. You have taught me the importance of vigorous research, dedication and firm belief in myself.

To Dr. Scott Grayson, thank you for being a mentor for both guidance in research and teaching me the principles of synthetic chemistry. It is through the numerous
conversations we shared that I was able to finally complete the synthesis of both polymers that were crucial to my thesis defense.

To my two brothers Saidi and Ahmed Baraka, and cousin Vincent Lutta, you truly kept me strong by continuously checking up on me and always pushing me towards success. The vacation trips we shared provided me with solace and allowed me to unwind and reflect on our future.

I would also like to thank my parents for raising me to possess a great desire for higher education. I firmly remember the quote my father always shared with me, “After all is lost, what is in your mind will determine how well you pick yourself up.” It is with great honor that I dedicate this Ph.D. to both Mohamed L. Baraka and Zohra A. Baraka for investing early on in my success and showing unconditional love.
# Table of Content

List of Figures ........................................................................................................... i

Chapter 1: Introduction .............................................................................................. i

1.1 Thermodynamics of BCPs ..................................................................................... 4

1.2 Impact of architecture on bulk self-assembly ...................................................... 8

1.2.1 Cyclic polymers ............................................................................................... 8

1.2.2 Star architecture ............................................................................................. 11

1.3 Thin films and confinement effects .................................................................... 12

1.3.1 Hard confinement .......................................................................................... 13

1.3.2 Soft confinement ......................................................................................... 14

1.4 Synthesis of block copolymers .......................................................................... 16

1.4.1 Anionic polymerization ............................................................................... 17

1.4.2 ATRP and radical polymerization .................................................................. 19

1.5 Self-assembly of BCPs ...................................................................................... 21

1.5.1 Thermal annealing ....................................................................................... 21

1.5.2 Solvent annealing ....................................................................................... 22

1.6 Membrane filtration ......................................................................................... 25

1.7 Thesis overview ............................................................................................... 27

Chapter 2 : The synthesis and self-assembly of poly(vinylmethylsiloxane-block-


 methylmethacrylate) (PVMS-b-PMMA) ................................................................. 29

1. Introduction ............................................................................................................. 29

2. Materials & Methods ........................................................................................... 33

2.1 Materials ........................................................................................................... 33

2.2 Instrumentation .................................................................................................. 33

2.3 Synthesis of PVMS-b-PMMA .......................................................................... 34

2.3.1 Synthesis of ω-Bromo-PVMS ...................................................................... 34

2.3.2 Synthesis of ω-azido-PVMS ....................................................................... 35

2.3.3 Synthesis of α –propargyl-ωBromo-PMMA by ATRP .................................. 35

2.3.4 Synthesis of PVMS-b-PMMA ...................................................................... 36

3. Results and discussion ....................................................................................... 38

3.1 Synthesis of PVMS-b-PMMA block copolymer ................................................. 38

3.2 Thin film studies ............................................................................................... 44
**List of Figures**

Figure 1-1 Typical phase diagram of a diblock copolymer. f: Volume fraction of one block. χ: Flory-Huggins interaction parameter. N: degree of polymerization. L: lamellae, H: hexagonally packed cylinders, Q\textsuperscript{230}: double-gyroid phase, Q\textsuperscript{229}: body-centered spheres, CPS: closed-packed spheres.\textsuperscript{7} .................................................................................................................. 3

Figure 1-2 (a) Two possible conformations of an A-B deblock and cyclic copolymer in the microphase-separated state characterized by a lamellar long-period A: bridged and single loop (c) Influence of χ*N upon domain spacing ratio of AB cyclic block copolymers and corresponding linear diblock copolymers in melts.\textsuperscript{32} .................................................................................................................. 10

Figure 1-3 Schematic of the A and B domains in the parallel (L\textsuperscript{||}), perpendicular (L\textsuperscript{\perp}) and mixed lamella (L\textsuperscript{M}) phases. Bold lines represent hard walls separated by a distance Δ₀. In the lower two illustrations, D represents the period of the lateral structure.\textsuperscript{47} ................. 14

Figure 1-4 Top views optical micrograph and side view schematic of a gradient thickness lamellar block copolymer thin film showing holes for thicknesses slightly less than the commensurability condition t = (n+0.5) × L₀, a featureless free surface near the commensurability condition, and islands for thicknesses slightly greater than the commensurability condition. Image reprinted from Albert thesis.\textsuperscript{49, 50} .................................................................................................................. 5

Figure 1-5 Illustration of anionic polymerization from the initiation, propagation, and termination steps .................................................................................................................................................................................. 19

Figure 1-6 Transition metal-catalyzed ATRP ............................................................................................................................................................................................................................................. 20

Figure 1-7 Solvent annealing procedure from (a) block copolymer deposited (b) substrate (c) film casting resulting in poorly ordered morphology (d) solvent (S) exposure to solvent swells film, (e) and deswelling by solvent evaporation. .................................................................................................................. 24

Figure 1-8 Solvent annealing setup while the film thickness is measured during swelling ............................................................................................................................................................................................................................................. 25

Figure 2-1 Synthesis of PVMS-b-PMMA block copolymer via a combination of ARGET-ATRP, anionic polymerization, and “click” coupling. Reagents and conditions (i) Anionic polymerization initiation by n-butyllithium and propagation using VD3 monomer. This is followed by termination with 11-bromoundecyldimethylchlorosilane for 2 hrs at room temperature under argon; (ii) End-group conversion with NaN\textsubscript{3}, DME, DMF 25 °C for 12 hrs; (iii) ATRP using Cu(I)Br, N,N,N',N",N" –pentamethyldiethylenetriamine (PMDETA), methyl methacrylate, 60 °C for 2 hrs; (iv) “Click” reaction with Cu(I)Br, N,N,N',N",N" –pentamethyldiethylenetriamine (PMDETA), dichloromethane, 25 °C .................................................................................................................. 32

Figure 2-2 NMR of characterization of homopolymers ω-bromo-PVMS, ω-azido-PVMS, PMMA, and finally the BCP PVMS-b-PMMA ............................................................................................................................................................................................................................................. 41

Figure 2-3 SEC curves showing shift increase in molecular weight from “click” chemistry, with other peaks depicting homopolymers. The blue curve shows well-controlled PVMS-b-PMMA, the red curve showing PVMS homopolymer, and the yellow curve showing
PVMS. The lack of peak broadening is an indication of the complete “click” reaction without side reactions. ..............................................................42

**Figure 2-4** Infrared spectroscopy showing the starting precursor functional group and the “click” reaction product. The peak at \( \approx 2100 \) cm\(^{-1} \) is an azide peak from the PVMS homopolymer, which disappears after the two homopolymers are reacted to form the diblock copolymer without any presence of starting material in the final BCP at the bottom image. .................................................................................43

**Figure 2-5** Traces of PVMS post polymerizing after end-group functionalization with azide. The black line corresponds to PVMS after 2-day storage, while the black line is PVMS post GPC measurement on the same day as reaction ended ........................................44

**Figure 2-6** AFM height images depicting the different morphologies from (a) thermally annealing PVMS-b-PMMA, (b) solvent annealing of PVMS-b-PMMA..............................45

**Figure 2-7** AFM images showing the morphological variation of PVMS-b-PMMA using a film swelling ratio (S.R.) of 1.3. As the solvent composition changes the morphology shifts from a poorly ordered morphology compromising of mostly parallel cylinders with only acetone (100 vol. %) to uniform perpendicular structure using a solvent composition of acetone/heptane (75:25 vol. %) ..........................................................................................................................48

**Figure 2-8** Impact of the swelling ratio of the films during SVA using a solvent composition of acetone to heptane 55:45 vol%. using a) 1.15 b) 1.3 c) 1.7.................................50

**Figure 2-9** 100 nm film thickness showed mixed morphology through film, but line cut showed domain spacing 13 nm ........................................................................51

**Figure 3-1** Synthesis of c-PVMS-b-PMMA from linear difunctional homopolymers \( \alpha,\omega \)-diazido-PVMS \( \alpha,\omega \)-bromo-PMMA. In the top most reaction \( \alpha,\omega \)-diazido-PVMS made using a combination of anionic and end-group substitution. \( \alpha,\omega \)-bromo-PMMA was created using ATRP and end-group substitution. Finally, c-PVMS-b-PMMA using “click chemistry)” ................................................................................................................56

**Figure 3-2** NMR characterization of homopolymers (a) \( \alpha,\omega \)-dihydroxy-PVMS, (b) \( \alpha,\omega \)-dibromo-PVMS (c) \( \alpha,\omega \)-azido-PVMS , (d) \( \alpha,\omega \)-dibromo-PMMA, (e) \( \alpha,\omega \)-propargyl-PMMA (f) cyclic PVMS-b-PMMA ..................................................................................62

**Figure 3-3** SEC graphs showing shift increase in molecular weight from “click” chemistry, with other peaks depicting homopolymers. The green curve shows well-controlled PVMS-b-PMMA, the red curve showing PVMS homopolymer, and the blue curve showing PMMA..........................................................................................................................65

**Figure 3-4** Infrared spectra of the synthesis of c-PVMS-b-PMMA, linear PVMS homopolymer and crude c-PVMS-b-PMMA with azide impurities from linear chains. The linear impurities are identified from the azide peak at 2100 cm\(^{-1} \).... ...........................................66

**Figure 3-5** NMR comparison between (a) n-butyl lithium initiated PVMS and (b) diphenylsilanediol initiated PVMS using anionic polymerization. The highlighted green region shows that VD3 initiation by n-butyl lithium results in two distinctive peaks, while initiation by diphenylsilanediol results in no peak........................................................................68

**Figure 3-6** Infrared spectra of end-group functionalized PMMA........................................................................69
Figure 3-7 IR spectra showing the effect of using a highly dilute (0.08 mg/ml) polymer concentration vs a more concentrate reaction solution. The presence of azide is indicative of either excess of one homopolymer or linear triblock homopolymer.

Figure 3-8 MALDI representation of PMMA before and after end-group conversion with bromide groups being present before and converted into amine groups with a change in relative Mn of 49 Da.

Figure 4-1 Optical image of the surfactant-stabilized a) water-in-toluene emulsion b) water-in-decane emulsion. The other images include water-in-oil emulsion mixtures in their respective containers for c) water-in-toluene and d) water-in-decane emulsions.

Figure 4-2 SEM images of PVMS coated membrane a) PVDF-200 b) PVDF-650 c) Cellulose.

Figure 4-3 Filtration experiments of water-in-toluene emulsion using the three different membrane type all coated with PVMS.

Figure 4-4 Filtration experiments of water-in-decane emulsion using the three different membrane all coated with PVMS.

Figure 4-5 Images of the filtrate collection of water-in-decane surfactant-stabilized emulsion after being purified by the following membranes a) PVDF-200 b) PVDF-650 c) Cellulose.

Figure 4-6 Dynamic light scattering images of the emulsion of a. water-in-oil emulsion and b. water-in-decane mixture.

Figure 4-7 NMR image to quantify the surfactant amount prior and after membrane filtration.

Figure A-1 Schematic showing the development of the nanoporous membrane.

Figure A-2 TEM images of etched PMMA from the solvent annealed PVMS-b-PMMA film (40 nm).

Figure A-3 Optical images of the emulsion of a. water-in-oil emulsion and b. water-in-decane mixture right after mixing and after being left for 24 hrs resulting in demulsification of water-in-toluene, while water-in-decane remains stable.
List of Tables

Table 2-1 Solvent collection measurements during solvent annealing........................................49
Table A-1 Library of the polymers synthesized using anionic, ATRP and "click" chemistry........................................95

List of Equations

Equation 1-1 Thermodynamic equation for calculating the Flory-Huggins interaction parameter from entropy and thermodynamic interactions.........................................................4
Equation 1-2 The interdomain period from strong segregation limit .................................................................9
Chapter 1: Introduction

Over the years, there has been an ever-growing demand for the development of new materials that produce the physical benefits of two or more separate materials. In the pursuit of such materials, several industries have utilized blending polymers. For example in the rubber industry, blending polypropylene and natural rubber showed good mechanical properties.\(^1\) The propylene allows for significant improvement in heat and ozone resistance, while the natural rubber retains bulk mechanical properties after vulcanization.\(^2\) Despite these physical benefits, polymer blends present an immediate challenge especially when dealing with highly incompatible polymers. However, even in apparently miscible blends, both nano and micro scale observations by microscopy have shown phase separation due to the enthalpic loss of bringing unfavorable materials adjacent to one another. When blending very incompatible polymers, it expected that the homopolymers will phase separate into two coexisting phases.\(^3\) In such scenarios, the gain in entropy from intermixing is far less than the enthalpic energy penalty from incompatible polymers interacting within the material. To mitigate such issues, the development of block copolymers was vital, given that the homopolymers have a covalent bond in between chain ends. This prevents complete phase separation of the copolymer blocks, while still allowing the individual chains to phase separate into nanoscale domains. Additionally, BCPs introduce the benefits of both physical and chemical properties of the individual homopolymer into one unit.\(^4\)
Block copolymers (BCPs) have garnered immense attention due to their inherent capability of conjoining two or more homopolymers to develop a new class of polymeric material. Creation of a permanent bond between polymer blocks prevents the usual macroscopic phase separation in inhomogeneous/incompatible blends. The benefits retained from using BCPs are well documented with several applications such as solar cells,\(^5\) drug delivery,\(^1\) nanoporous membrane,\(^2,3\) nano-templating,\(^4\) and organic optoelectronics.\(^5\) Self-assembly is governed by several parameters such as the degree of polymerization (N), volume fraction (f), and Flory-Huggins interaction parameter (\(\chi\)). These factors contribute to the phase behavior of AB diblock copolymer with morphological shifts directly affected by each independent variable. The equilibrium phase behavior of the bulk polymer has been studied both experimentally and theoretically.\(^6\) This work identified morphologies such as the lamellar (L) phase, in which domains form alternating layers, the cylinder (C) phase, where the minority block forms cylinders, and finally, the sphere (S) morphology, with the minority block forming spheres.\(^6a,7\) Furthermore simulation improvement by Matsen and Schick\(^8\) then came to introduce other unknown complex phases such as gyroid (G) and perforated-lamella (PL).
Figure 1-1 Typical phase diagram of a diblock copolymer. $f$: Volume fraction of one block. $\chi$: Flory-Huggins interaction parameter. $N$: degree of polymerization. L: lamellae, H: hexagonally packed cylinders, $Q^{230}$: double-gyroid phase, $Q^{229}$: body-centered spheres, CPS: closed-packed spheres.\textsuperscript{6b}
1.1 Thermodynamics of BCPs

Block copolymer self-assembly can be dated over 30 years ago with published work from Leibler and Helfand,\(^7,9\) Both of whom described the Flory-Huggins interaction parameter \(\chi_{AB}\) between individual chains as the driving force towards polymer chain segregation. The interaction parameter is understood as the free energy cost per monomer of conjoining two blocks. Thus, positive, \(\chi_{AB}\) (which is most common in block copolymers) results in greater phase separation; whereas a negative value signifies complete mixing of unlikely polymers.

Equation 1-1: Thermodynamic equation for calculating the Flory-Huggins interaction parameter from entropy and thermodynamic interactions

\[
\chi_{AB} = \chi_S + \frac{\chi_H}{T}
\]

In the above equation, \(T\) refers to the temperature in Kelvin units, \(\chi_S\) is the entropic parameter resulting from intermixing monomers, with \(\chi_S\) being an enthalpic contribution towards phase separation. As earlier stated, entropy affects the polymer chains ability to intermix randomly. Additionally, the enthalpic energy driving the chains to separate is usually large in magnitude and has more impacts on the phase separation capabilities of the BCP. The enthalpic parameter is driven by chemical dissimilarities and polarity differences in the molecules. This results in scenarios where even small chemical disparities such as isotopes of a molecule, polystyrene, and deuterated-polystyrene, have demonstrated large immiscibility at sufficiently high molecular weight.\(^7\)
In designing block copolymers for several applications, we refer to the phase diagram in Figure 1-1 for developing the desired morphology. The most effective synthesis techniques are utilized to obtain the desired composition (f) and molecular weight (N). The molecular weight affects the ability of the chains to either intermix or phase separate at a given $\chi_{AB}$, which is dictated by the chemistry of the chosen polymers. As observed from the phase diagram, an increase along the vertical axis will result in a transition from disordered-to-order morphology. The individual polymers used will predetermine the segregation strength with the final BCP categorized as strongly segregated, weakly segregated, or of intermediate segregation strength. Polymers located in the weakly segregated ($\chi_{AB}^* N \approx 10$) domain tend to form poorly ordered nanostructures. In this region, the block copolymer is either of low molecular weight or weakly phase separated resulting in a disordered structure. As a result, the interfacial width tends to be broad due to individual polymer chains permeating into each other’s domains. This region is usually identified by the order-to-disorder transition. As the segregation number ($\chi_{AB}^* N$) increases – either by tuning molecular weight or Flory-Huggins parameter- a more distinct boundary between interfaces is obtained. This region on the phase diagram is identified as the intermediate segregation regime ($10 < \chi_{AB}^* N < 100$). This region provides for new additional phases such as the double gyroid which lies between the lamella and cylinder phases. Finally, the strong segregation limit (SSL) operates when $\chi_{AB}^* N > 100$ in this region complete phase separation results in narrower interfacial widths. In synthesizing BCPs, calculation of the $\chi_{AB}^* N$ is needed to achieve the desired morphology and phase separation.
In our lab, we primarily focus on using polymers that phase separate in the intermediate to strong segregation regimes. We emphasize on this region not only due to the increased number of morphologies but also due to the reduced inter-domain spacing between blocks brought by shorter chains (N) that allow for potential several industrial applications in the polymer industry. Semenov\(^\text{10}\) predicted the inter-domain period in the SSL to follow the equation below:

Equation 1-2: The Interdomain period from strong segregation limit

\[ d = \alpha N^{2/3} \chi^{1/6} \]

where: \( d \) signifies domain spacing, \( \beta \) signifies proportionality constant, \( \chi_{AB} \) signifies Flory Huggins parameter, and finally \( N \) signifies Number of repeat units in the chain.\(^\text{10}\)

The number of repeat units (N) has a more pronounced effect on the domain spacing than \( \chi_{AB} \). This results in developing materials with large enough Flory Huggins parameters (\( \chi_{AB} \)) to allow for phase separation, and smaller molecular weights that result in smaller feature sizes. Additionally, the magnitude of \( \chi_{AB} \) will impact phase separation and interfacial roughness due to a large driving force toward separation.\(^\text{11}\) Historically, poly(styrene-b-methyl methacrylate) (PS-b-PMMA) has been the industry standard to for creation of nanostructured templates because it is easily oriented by varying annealing temperature and etching of PMMA after self-assembly, and this has well been documented.\(^\text{66}\) However, the compatibility between the monomers limits the ability to further drive the domains into smaller lengths scales. The small phase separation
parameter for PS-b-PMMA, $\chi \approx 0.03$, limits the pitch size of the polymer to $\approx 24$ nm.\textsuperscript{12} Although this feature size is smaller than that produced by traditional light-based lithography techniques, recent advances in light-based lithography techniques have pushed feature sizes even smaller. However, bottom-up approaches, such as block copolymer templating, still offer a potential route to further reducing feature sizes to sub-10 nm and doing so more economically than light-based techniques. This reduction in pitch size is fundamentally important for technology companies to continue following Moore’s law of increasing the number of transistors per microchip.\textsuperscript{13}

For BCPs to phase separate at low pitch sizes, the incompatibility of the monomer units must be increased leading to improved long range-order and reduced line edge roughness. In pursuing such measures, shorter BCPs incorporating inorganic material is needed.\textsuperscript{11} Park et al.\textsuperscript{14} demonstrated that incorporating organosilicates nanoparticles into a block copolymer resulted in improving phase separation with pitch sizes below 10 nm. In this experiment poly(styrene-b-ethylene oxide) PS-b-PEO (5.1 kg/mol) was used given the high phase segregation already in place. However, the addition of the organosilicate improves the ability to proceed to smaller feature sizes as a result of the organosilicate migrating completely into the polar/similar characteristics as PEO. This work followed a long series of publication looking at the impact of nanoparticles in self-assembly with BCPs.

The mechanism that the nanoparticles localize in the polymer domain is divided into several categories such as (i) selective localized in the center of selective polymer domain (ii) uniform distribution (iii) localized along with the interface.\textsuperscript{15} The improved
capability to achieve smaller domains is both a beneficial and deterring process. The process is undesirable at times when the nanoparticles result in the introduction of undesired impurities and present a challenge in removing them post-self-assembly. To mitigate issues with blending material, synthesizing inorganic-organic block copolymers is proving highly desirable. This has then led to a push towards using newer and improved synthesis techniques to develop inorganic-organic BCPs.\textsuperscript{16}

Prior limitations in synthesis techniques prevented the formation of hybrid polymers. However, using more modern approaches to make pristine silicon-containing block copolymers with high degree of incompatibility is possible.\textsuperscript{14, 17} Apart from the large interaction parameters, such polymeric systems possess natural contrast to allow for facile pattern transfer to the substrate with oxygen plasma etching.\textsuperscript{18} Polydimethylsiloxane (PDMS) is a very low surface energy material with the pendent methyl group allowing for chemical stability and chemical resistance.\textsuperscript{19} Jung et al.\textsuperscript{20} reported the formation of an array of parallel cylinders with 8 nm diameter for a polymer with an overall molar mass 16 kg/mol. The same PDMS substituent was shown to allow 6 nm cylinder diameter with pol(2-vinylpyridine), and later work also shows molar masses lower than 3.9 kg/mol still formed microphase-separated nanostructures.\textsuperscript{17a, 21}

1.2 Impact of architecture on bulk self-assembly

1.2.1 Cyclic polymers

The linear diblock copolymer is one of the most studied architectures in block copolymer literature, primarily due to its phase diagram being well-developed.\textsuperscript{7} However, several other architectures are possible such as star, triblock, cyclic BCPs and are gaining
prominence.\textsuperscript{22} Earlier theories have shown that the phase transition of BCPs is driven by a tendency to curve the interface as the composition becomes asymmetric. This allows for the chains to retain the ideal configuration between stretching and compression.\textsuperscript{4} In addition to composition, polymer architecture also affects the morphology by allowing for a variety of configurations, based on the number of arms,\textsuperscript{22} branches,\textsuperscript{22-23} interconnecting blocks, and end-groups.\textsuperscript{24}

Cyclic block copolymers are a unique class of polymers lacking any end-group functionality. The BCP upon nanophase separation has shown to have smaller feature sizes, with a 30 % reduction compared to linear analogs of the same molecular weight.\textsuperscript{25} During the segregation, the individual blocks form loops in their respective domains and the two junction points between the blocks reside at the interface.\textsuperscript{26} This results in smaller and more compact packing of the chains. In comparison to their linear analogs which conform to a bridge assembly - both chains end in their respective domains - cyclic BCPs form a double-loop structure resulting in reduced domain spacing (Figure 1-2).\textsuperscript{27} The reduction in feature size is relevant especially in the development of lithographic templates, where a continuous drive to designing small features is hindered by an inability to self-assemble low-molecular-weight polymers.\textsuperscript{17b} \textsuperscript{28} Furthermore, cyclic BCPs are relevant in other fields such as drug delivery, lubrication, and emulsion stabilization.\textsuperscript{29} Hoskins and Grayson\textsuperscript{30} showed different degradation rates between cyclic and linear analogs of poly(caprolactone), with the former proving to have a delay in degradation rates. The lack of chain ends in the polymer allows the backbone to retain a linear chain structure upon degradation, whereas the linear chain completely disintegrates into two
chains upon exposure to a stimulus with each degradation resulting into a shorter chain polymer. The degradation of the cyclic polymer might be used as a stimuli-responsive control for drug delivery.\textsuperscript{30} In the lubrication industry, cyclic block copolymers are relevant due to the low intrinsic viscosity.\textsuperscript{31} The lack of chain ends mitigates entanglement between polymer chains. Hence, the response of the polymeric chain to shear force differs from the linear counterpart.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1-2.png}
\caption{(a) Two possible conformations of an A-B deblock and cyclic copolymer in the microphase-separated state characterized by a lamellar long-period A: bridged and single loop (b) Influence of $\chi^*N$ upon domain spacing ratio of AB cyclic block copolymers and corresponding linear diblock copolymers in melts.\textsuperscript{27}}
\end{figure}

In addition to viscosity, the lack of chain ends will contribute to the deviation of the thermal properties such as melting temperature ($T_m$) and glass transition temperature ($T_g$).\textsuperscript{32} Zhang and Torkelson were able to show the impact of chain ends on the glass
transition of confined thin films of both linear and cyclic polymers. Using different initiators to synthesize low molecular weight polystyrene, nitrogen atoms in the chain ends interact with Si/SiO$_x$ substrate. Competing effects between free-surface (polymer-air interface) and the polymer-substrate interface can readily tune the magnitude of $T_g$. For example, linear polystyrene (PS) on silica substrates exhibit a decrease in $T_g$ with decreasing thickness due to the strong free-surface effects and absence of strong interactions at the substrate interface. Additionally, the development of various polymeric coatings which require thermal stability may benefit directly from the reduced fragility of cyclic polymers. Fragile materials are understood to show abrupt changes in the physical properties when they approach the $T_g$; hence fragility can also be a measure of a polymer structural stability.

1.2.2 Star architecture

In addition to cyclic polymers, different architectures such as the star copolymers contribute to the thermodynamic stabilization of unique morphologies. For example, bulk films developed by star copolymers stabilizes new morphologies such as bicontinuous cubic morphology; whereas linear architecture would create lamellae. The inclusion of several junctions in the star architecture is significant in furthering polymorphism of the phase diagram. The star copolymer consists of a core-shell polymer with 3 or more homopolymer chains attached. The self-assembly of star chains are governed by increased stretching free energy as the arms move away from the interface; reduction of interfacial energy; and increased entropic from delocalizing polymeric coils at the
interface.\textsuperscript{36} Lo et al. \textsuperscript{37} were able to circumvent the difficulties from wetting the interface by lower surface energy individual domains in BCP thin films by using star deblock copolymers. The high entropic penalty with localizing the star polymer chains on the substrate far outweighs the enthalpic gains of phase separation, hence star copolymer will conform to a surface-neutralizing perpendicularly oriented morphology.

1.3 Thin films and confinement effects

The field of block copolymers has rapidly expanded over the course of several years with a well-established phase diagram dictating the impact of composition, polymer-interaction ($\chi$) and molar mass on self-assembly. \textsuperscript{7} However, the phase diagram fails to recognize the effects that BCP thin films (~10-200 nm) endure in comparison to the bulk morphology such as surface interactions and confinement due to film thickness.\textsuperscript{38} Surface interactions may shift the orientation of BCP nanostructures from parallel to perpendicular or vice versa. Additionally, surface interactions have been shown to alter the morphology based on the preferential interaction of individual chains onto either substrate or surface.\textsuperscript{7}

The confinement of block copolymer is observed when the film thickness is less than $6xL_0$.\textsuperscript{66} This affects the ability of chains to stretch or compress to an energetically favorable structure that relieves the entropic penalty of constraining the domains with an increased enthalpic interaction at the substrate.\textsuperscript{39} The confinement can be categorized into either: (1) hard confinement, which is where the polymer is under constant contact with two surfaces at all times (2) soft confinement which occurs when the BCP is on contact with both a substrate and the other side is free-surface (atmosphere).\textsuperscript{38}
1.3.1 Hard confinement

During hard confinement, the polymer film is confined between two materials, which may be similar or different. Interactions may be symmetric, where the individual block A segregates to both interfaces upon annealing, or asymmetric, where block A segregates to one of the interfaces and block B segregates to the opposite interface. It should be noted that asymmetric wetting only occurs when using two different materials of varying surface energies for hard confinement.

In scenarios of no preferential interaction between substrates and polymer, the acceptable orientation would be perpendicular to the walls. Experiments on confined films have shown frustration in the parallel orientation are relieved once the film switches towards a perpendicular orientation. The explanation is that the repeat unit ($L_0$) is free to relax to the bulk spacing ($L_B$). The relaxation can result in a mixed orientation ($L_{V^M}$) of both parallel and perpendicular lamella if one interface is preferential for a block and the other interface is neutral, or non-preferential (Figure 1-3). An enthalpic penalty is observed by having two different orientations across an interface. However, this is compensated by the lower surface energy with parallel lamella and reduce chain stretching and compression. Despite the mixed morphology being slightly unfavorable, highly incommensurate lamella films are the driving force towards the orientation.
1.3.2 Soft confinement

The exposure of thin films to the free-surface and one substrate allows for chain stretching/relaxing to alleviate incommensurability between the film thickness ($t$) and the polymer domain spacing ($L_0$). Irregular microstructures known as island/holes are formed based on incommensurate conditions between film thickness and polymer domain spacing (Figure 1-4). In situations of neutral interactions between surface and substrate,
the BCP will orient perpendicular to the surface. The definition of commensurability is guided by both differences in film thickness (t) and domain spacing (L₀), also combined with surface interaction between polymer and substrate. For a lamella AB block copolymer with block A preferring to wet both free-surface and substrate this is known as symmetric wetting; whereas if block A wets the substrate and block B prefers the free-surface this is known as anti-symmetric wetting. For symmetrical wetting of block A, commensurability conditions are met when \( t/L₀ = n \) (\( n = 1,2,3, \ldots \)), the BCPs chains are in their most stable condition. Additionally, for anti-symmetrical wetting the conditions for commensurability are \( t/L₀ = n + 0.5 \) (\( n = 1,2,3, \ldots \))

Figure 1-4 Top views optical micrograph and side view schematic of a gradient thickness lamellar block copolymer thin film showing holes for thicknesses slightly less than the commensurability condition \( t = (n+0.5) \times L₀ \). Image reprinted from Albert thesis.
Several groups have tried to control the regularity of the island/hole formation by epitaxy.\textsuperscript{42} Rockford et al.\textsuperscript{42a} developed periodic templated surfaces on a substrate prior to casting a film. By casting a symmetrical composition polymer, they can control the lateral separation and long-range formation of island/holes. Additionally, Heier et al.\textsuperscript{42b} were able to alter the surface of BCPs by the method of chemoepitaxy. This involved chemically patterning on a surface with length scale 1-16 $\mu$m to induce island/hole formation.\textsuperscript{38}

1.4 Synthesis of block copolymers

The synthesis of polymers is the primary tool that allows for the development of various polymeric architectures, composition, and functionality. Various methods have been used for making polymers such as chain growth and condensation polymerization. Chain growth polymerization is used due to its ability to effectively control the molecular weight and polydispersity.\textsuperscript{43} In the process of chain growth polymerization, the three processes involved include (1) initiation using a catalyst, radical initiating agent and/or energy (2) propagation and (3) propagation. As we have seen from the phase diagram, the total molar mass affects the segregation strength ($\chi^*N$), which will determine whether the block copolymer self-assembles. Additionally, polydispersity has proven to also play a distinctive role in stabilizing or leading to new morphologies that were otherwise not stable equilibrium structures.\textsuperscript{43} Apart from that, polydispersity also affects the interfacial width of the individual polymer. Shorter chains are more adversely impacted by
translational entropy due to the confinement of the films and as a result, will have broader interfacial width.\textsuperscript{44}

Condensation polymerization is also heavily used in developing homopolymers, based on the reactivity of the pendant reactive ends of the monomer starting materials. In this reaction a small molecule is usually produced as a byproduct, hence the name condensation polymerization. The major disadvantage of condensation polymerization is the lack of ability to control both polydispersity and chain length. The control of polymerization becomes crucial and in this thesis, we focused on using chain growth polymerization by means of using both anionic and atom transfer radical polymerization to synthesize the desired BCP.

1.4.1 Anionic polymerization

Anionic polymerization is defined as a chain-growth polymerization that generates negatively charged species at the end of the homopolymer/block copolymer, making it still reactive and able to combine further with other monomers to increase chain length. This method has been used for several years for manufacturing various polymers such as linear, star and triblock copolymers. The polymerization proceeds in three sequential steps. The first step involves initiation where the anions are first produced through the reaction of a strong anion/base with a monomer. This is usually the rate-limiting step with poor efficiency of initiator or side-reaction with impurities dictating the final molecular weight. After the initiation step, the reaction progresses through further collisions
between the anion on the propagating chain and additional monomers. In the final termination step, the anion is converted into neutral species by reaction with proton usually from either an acid or water (Figure 1-5). Anionic polymerization is considered a “living” polymerization due to the absence of chain terminations during propagation and irreversible intermolecular chain transfer being absent. Chain transfer occurs when the activity of the growing chain is transferred to another molecule. For example, a charged polymer loses its charge to a neutral homopolymer/monomer species. The lack of termination allows for the synthesis of polymer with control of both molecular weight, molecular weight distribution, copolymer composition and microstructure, stereochemistry, chain-end functionality, and molecular weight architecture. As a result of this, anionic polymerization is one of the most used industrial technique to develop industrial polymers such as poly(styrene-b-isoprene-b-styrene) (SIS), polyisoprene, polybutadiene and many more.
1.4.2 ATRP and radical polymerization

Atom transfer radical polymerization (ATRP) is a controlled radical polymerization that allows for reaction to take place by eliminating irreversible chain transfer and chain termination.\(^{46}\) It is one of the most versatile and heavily used methods of synthesizing polymers of complex architectures, chain length, and dispersity.\(^{47}\) The concept of ATRP is to slow uncontrolled radical polymerization by inserting intermediate activation-deactivation steps during polymerization. By inserting multiple reversible radical deactivation steps, well-defined polymers are achieved.\(^{48}\) Additionally, ATRP allows for the rate of propagation to be 1000 times faster than that of termination; this allows for
the development of a high degree of polymerization. During the reaction, there are two key properties for successful synthesis: (1) efficient initiation of the polymer initiator (2) reaction conditions minimize irreversible terminating chains by controlling the number of free radicals present in solution.\textsuperscript{48} A general synthesis method of ATRP is observed in Figure 1-6.

\[
R\cdot X + M_t^n\cdot Y / \text{Ligand} \xrightarrow{k_{\text{act}}} R^* \xrightarrow{k_{\text{deact}}} \quad X-M_t^{n+1}\cdot Y / \text{Ligand}
\]

Figure 1-6. Transition metal-catalyzed ATRP.\textsuperscript{49}

In this initiation step, the alkyl halide species (R\cdot X) reacts with a complexed metal catalyst (M_t^n – Y, usually copper(I)) with a rate constant of activation (k_{\text{act}}) to produce an intermediate radical (R\cdot). The transition metal complexes into a lower oxidation state (X-M_t^{n+1} – Y). The propagation of the polymer is followed by reacting with individual monomer chains and further growing the chain length with a constant rate of propagation (k_p). Finally, the termination occurs by deactivating the radical by reacting with a higher oxidation metal with a constant rate of termination (k_t) (Figure 1-6).\textsuperscript{49}

In comparison to other polymerization techniques, ATRP differentiates itself from anionic or cationic polymerization with the benefits of greater tolerance towards functional groups in the monomer/homopolymer, oxygen, and water. This makes it one of the most robust polymerization techniques available. Since its discovery, ATRP has
grown to be used in several applications such as biocompatible polymers, protein-polymer conjugates, DNA, and surface-initiated polymerization.

Further improvements to ATRP by addition of a reducing agent such as tin (II) 2-ethylhexanoate, ascorbic acid, or hydrazine allows for continuous regeneration of the copper (I) \((M_t^n - Y)\) after oxidation from copper (II) \((M_t^{n+1} - Y)\). This method, known as Activator ReGenerated by Electron Transfer (ARGET) ATRP, is proven to be less susceptible to oxygen or water. Additionally, minimizing the amount of copper in the reaction results in improved functionality by reducing the occurrence of catalyst-based side reactions (β-H elimination). In conventional ATRP, chain-end functionality is lost due to termination reactions between growing radicals and a copper catalyst.

1.5 Self-assembly of BCPs

Casting of polymeric films onto a substrate usually leaves the chains in a kinetically trapped nanostructure. For the polymers to obtain thermodynamically favorable morphology and orientation, the polymer chains require mobility to shift orientation and morphology. The two common processing techniques involve thermal and solvent annealing to impact orientation and morphology.

1.5.1 Thermal annealing

For thermal annealing, the polymer is heated above its glass transition temperature. The chains gain enough energy to mobilize them, hence moving towards the most energetically favorable orientation. This is the most favored technique used
both industrially and in academia due to the simplicity of adjusting only two variables: the annealing temperature and annealing time. Polymers with low surface energy tend to segregate to the free-surface. Additionally, similar chemistry functionality and polarity dictate the polymers ability to wet the substrate.\textsuperscript{36b, 55} However, according to Eotvos rule, the surface tension of liquid decreases with the increase of temperature.\textsuperscript{56} Hence, polymers with relatively close surface energies such as PS-\textit{b-PMMA} can have the same surface tension upon thermal annealing at the correct temperatures. This will allow polymers to retain a perpendicular cylinder by thermal annealing. For example, PS-\textit{b-PMMA} is used above $\approx 170$ °C to 230 °C, the surface energies become comparable.\textsuperscript{57} Despite the benefit of simplicity, thermal annealing is avoided for temperature sensitive materials that may degrade at even moderately elevated temperatures.

1.5.2 Solvent annealing

In this process, the polymer is exposed to solvent vapor, which lowers the $T_g$’s of the copolymer blocks to allow for equilibrium structure to form a more moderate temperature, usually at room temperature. The polymer expands as the solvent permeates through the film, promoting chain mobility. After exposure for certain periods of time the solvent evaporation rate can be used to tune the well-organized nanostructure (Figure 1-7).\textsuperscript{58} Unlike thermal annealing, this is a cold processing technique that can occur at ambient temperature. Solvent annealing mitigates any issues regarding thermal degradation and excessive long anneal times of high molar mass polymers.\textsuperscript{57}

Prior to solvent annealing, the $T_g$’s of the component blocks and surface tensions must be considered and their preference to individual solvents as this will play an integral
role in the final morphology. Polymers tend to have different states at ambient conditions such as glassy, amorphous, and liquid. Each physical state will interact differently with solvent and impact the solvent uptake and ultimately the rearrangement during solvent annealing. Apart from the physical state, the volume fraction of the blocks must be taken into account especially when performing solvent annealing. Paik et al. were able to show an order-order transition occurred due to the solvent shifting the volume fraction of the individual polymers. During solvent annealing two key parameters are affected during swelling: (1) effective \( \chi \) parameter, and (2) volume fraction. During solvent annealing, neutral and good solvents will compatibilizer in both domains, while preferential in only one domain. It is imperative to have an understanding of how the solvent type and swelling ratio (swollen state thickness during the annealing/initial thickness) will impact the BCPs orientation and morphology. The setup for the solvent annealing is illustrated on Figure 1-8.
Figure 1-7 Solvent annealing procedure from (a) block copolymer deposited (b) substrate (c) film casting resulting in poorly ordered morphology (d) solvent (S) exposure to solvent swells film, (e) and deswelling by solvent evaporation.59
1.6 Membrane filtration

The Deepwater Horizon explosion resulted in several million barrels of oil being spilled into the Gulf of Mexico. During the remediation process, several lapses in finding an effective way to separate the water-in-oil led to dispersants being employed into the water further degrading the environment and ecosystem. For example, dioctyl sodium sulfosuccinate (DOSS) which was thought to undergo rapid degradation post-recovery is still present in the environment and can persist for over 4 years.\textsuperscript{62} This has led to several important questions regarding effective methods of remediating and separation of water-in-oil mixtures.\textsuperscript{63} In finding an effective technology it must satisfy several conditions such as high purity, efficiency, continuous processing, and chemical inertness.
For oil spill remediation, several technologies such as chemical precipitation, skimming, dispersants, and membranes have all been deployed either individually or in combination. Despite this, membrane filtration provide advantages such as low operating temperatures, simple operation processes, low energy consumption, high efficiency, and a small investment making it a more viable separation method.\textsuperscript{64} Membrane design for water-in-oil emulsion separation requires optimizing of: (1) selectivity of the desired component (2) surface porosity, which affects the rate of permeation through the membrane, and (3) breakthrough pressure ($P_{\text{breakthrough}}$), which is maximum pressure difference across the membrane in which the undesired phase flows through.\textsuperscript{65} The surface porosity also plays a fundamental role in size discrimination of various molecules larger than the pore size. Additionally, depending on the pore diameter of the membrane, it can allow the one-dimensional flow of particles diffusion through the narrow channel.\textsuperscript{66}

For oil-water separation, the chemical functionality on the membrane walls impact the operation conditions. In selecting hydrophilic membranes for filtration, the inhibiting factor is high fouling in the membrane walls that later affect separation efficiency and flux through the membrane.\textsuperscript{67} Numerous approaches have been employed to eradicate biological material from being absorbed on the surface by chemical modification with fluorinated compounds.\textsuperscript{68} The relatively low surface energy of the fluorine chemical moieties compared to aliphatic groups in the order: $-\text{CH}_2$ (36 mN·m$^{-1}$) $> -\text{CH}_3$ (30 mN·m$^{-1}$) $> -\text{CF}_2$ (23 mN·m$^{-1}$) $> -\text{CF}_3$ (15 mN·m$^{-1}$) has resulted in fluorine coating being well incorporated for antifouling and anti-stick purposes.\textsuperscript{69} In addition to low surface energy, the chemical robustness of fluorinated coatings allows for harsh
conditions use. For example, polytetrafluoroethylene (PTFE) is used in kitchen appliances, paint, and various other situations. However, the disadvantage of using fluorinated materials is that surface irregularities promote the accumulation of biofouling on the surface. In this situation, the biological substance invades the crevices and curves on the surface and creates secure mechanical interlock. In selecting a silicone based coating, the anti-fouling is enhanced.

Anti-fouling release is an important characteristic that influences the capability of a material to be an effective membrane. Antifouling involves fracture between two surfaces such as the membrane and foulant. The mechanism can involve peeling of the two materials by in-plane shear and finally out-of-plane shear. Brady et al. described that low foulant adhesion correlates with low elastic modulus because the membrane is easily deformable and this allows for molecules to shear away off the surface. The most common method of removal of biomolecules from silicone substrate involves deformation, followed by peeling off. This requires less energy than detachment by shear or tension. Hence, the desire to find an effective anti-fouling coating, while still retaining hydrophobicity will involve using a siloxane-based polymer.

1.7 Thesis overview

This thesis focuses on the use of silicon-based polymers to induce phase separation of polymers at a low molecular weight. The evolution of knowledge in the polymer field both in terms of polymeric architecture and polymer synthesis has ushered
the 21st century into new heights of (1) smaller dimension in BCPs, (2) new morphologies development into the BCP phase diagram. In this thesis, I use robust synthesis techniques such as ARGET-ATRP and “click” chemistry to co-join homopolymers in order to make monodisperse and well-controlled molecular weights for BCPs. After the polymerization, I induced self-assembly by both thermal and solvent annealing to capture different orientations. The thin film studies were observed by atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Finally, I successfully synthesized cyclic BCPs containing a silicon-based block with the aim of later studying the impact of polymer architecture on morphology.

A more detailed description of the synthesis techniques is provided in chapter 2 that involves using poly(vinylmethylsiloxane-block-methylmethacrylate) (PVMS-b-PMMA) to characterize self-assembly of the BCPs using either thermal and solvent annealing. Chapter 3 deals with the efficient synthesis of cyclic PVMS-b-PMMA with the goal of having high purity and yield. Finally, Chapter 4 discusses the development of hydrophobic coating on microporous membranes for oil recovery from water-in-oil emulsions.
Chapter 2 : The synthesis and self-assembly of poly(vinylmethylsiloxane-block-methylmethacrylate) (PVMS-b-PMMA)

Silicon-based block copolymers have gained attention because of their ability to self-assemble at the low molecular weight. By utilizing this important factor, we synthesized a poly(vinylmethylsiloxane-block-methyl methacrylate) (PVMS-b-PMMA) with the aim of creating narrow pores with potential application in nanolithography and/or membrane filtration. The polymer is made by a combination of anionic synthesis of PVMS, ATRP of PMMA, and then joining the end-group functionalized homopolymers with a click reaction to form PVMS-b-PMMA. After synthesis, continuous nanopores aligned mostly perpendicular to the substrate have then developed solvents that create a neutral free-surface by co-solvent solvent annealing. Additionally, we observed morphological changes resulting from different swelling ratios and co-solvent compositions

1. Introduction

Over the past decades, the self-assembly of block copolymers (BCPs) in thin films has attracted enormous attention in various applications such as drug delivery,\textsuperscript{50} nanoporous membranes,\textsuperscript{73} nano-templating,\textsuperscript{74} and organic optoelectronics.\textsuperscript{75} The inherent ability of the individual chains to self-assemble into the desired morphology with each polymer segment having specific chemical/physical properties has led to the great
use of BCPs. In the lithographic industry, BCPs provide an advantage as a robust next-generation technique with the ability to control properties such as orientation, morphology, and small feature size. For membrane separation, BCPs are highly utilized as a result of lower operating cost and higher selectivity in processes such as gas and water transport, filtrations of viruses, and separation of water-organic solvents. While in operation, BCP membranes provide ultrahigh selectivity for separation of viruses, emulsion, and nanoparticle filtration. This is a result of size discrimination of the porous membrane based either on the molecular weight or particle size during filtration.

In utilizing block copolymer self-assembly, several desired characteristics can be achieved, including: (1) defect-free selective layers; (2) intrinsic porosity that is comprised of sub-10 nm pores, and (3) rigidity to prevent thermal and solvent expansion and contraction of pores. The sub-10 nanometer voids provide the greatest advantage due to their ability to allow single-file diffusion. Single-file diffusion (SFD) is a one-dimensional (1D) diffusion that occurs when diffusing particles pass through a narrow channel. Industrially, SFD is utilized in the separation of protein drugs through membranes, whereby diffusion through the channel is constant despite changes in time and concentration. Yang et al. demonstrated the constant release of bovine serum albumin (BSA) in vitro. This was possible by carefully controlling the pore diameter to a size similar or close to the hydrodynamic radius of BSA, hence improving the molecular interaction between the solute and the polymer membrane. Akthakul et al. attributed the strong-hydrogen bonding ability of the side chains on the polymer membrane for allowing water
molecules to permeate while rejecting the adsorption of oleophilic material to the membrane surface. Despite the work on separating oil-water mixtures, more effort should be focused on separating nanoemulsions, i.e. oil-water mixtures containing sub-micron droplets.

To address this need, this work focuses on the synthesis of a new class of hydrophobic nanochannel membranes with a primary emphasis on using small feature templates for ultrafiltration membranes and lithographic templates. As noted previously, BCPs allow for self-assembly to a desired cylindrical nanostructure based on volume fractions. A facile synthesis technique is used to combine the end-group functionalized homopolymers to develop an inorganic BCPs with high Flory-Huggins (χ) parameters, that self-assemble to the sub-10 nm length scale. In this paper, we aim to create a hydrophobic membrane by utilizing polymer self-assembly of incompatible, low-molecular-weight block copolymers and selectively etching one of the polymer blocks. We utilize poly(vinylmethylsiloxane) (PVMS) due to its low surface energy that allows for great hydrophobicity in the BCP poly(vinylmethylsiloxane (PVMS)-block-methyl methacrylate) (PVMS-b-PMMA). Additionally, the PVMS homopolymer’s physical characteristics make it highly incompatible with organic homopolymers such as PMMA, hence driving greater phase separation. This allows for the development of sub-10 nm feature sizes. Additionally, using PVMS, instead of the more common poly(dimethylsiloxane) (PDMS), allows for surface modification via chemical and physical treatment. In addition to the benefit of easy modification of the PVMS surface,
chemically cross-linking PVMS instead of PDMS would allow for a more robust and mechanically stable material.

Figure 2-1 Synthesis of PVMS-b-PMMA block copolymer via a combination of ARGET-ATRP, anionic polymerization, and “click” coupling. Reagents and conditions (i) Anionic polymerization initiation by n-butyllithium and propagation using VD3 monomer. This is followed by termination with 11-bromoundecyldimethylchlorosilane for 2 hrs at room temperature under argon; (ii) End-group conversion with NaN₃, DME, DMF 25 °C for 12 hrs; (iii) ATRP using Cu(I)Br, N,N,N’,N”,N”-pentamethyldiethylenetriamine (PMDETA), methyl methacrylate, 60 °C for 2 hrs; (iv) “Click” reaction with Cu(I)Br, N,N,N’,N”,N”-pentamethyldiethylenetriamine (PMDETA), dichloromethane, 25 °C
2. Materials & Methods

2.1 Materials

All reagents were used as received from chemical vendors unless otherwise indicated. Tetrahydrofuran (THF) was dried with a solvent purifying system from Mbraun (MB-SPS-800). 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (VD3) and 11-bromoundecyldimethylchlorosilane were both purchased from Gelest. The following reagents were purchased from Sigma-Aldrich: n-butyl lithium solution in hexane (2.5 M); sodium azide ( NaN₃); dimethylformamide (DMF); dimethoxyethane (DME); propargyl-2-bromoisoobutyrate, N,N,N’,N”’,N”'-pentamethyldiethylenetriamine (PMDETA); copper(I)bromide (Cu(I)Br); methyl methacrylate (MMA); and tin (II) 2-ethylhexanoate (Sn(EH)₂). Poly(vinyl acetate) (40% hydrolyzed) was purchased from Polymer Sciences. Finally, methanol from EMD Millipore and dichloromethane from BDH were used as received.

Prior to the synthesis, VD3 monomer was freeze/pump/thawed under argon and dried overnight on molecular sieves (Fisher Scientific). MMA was run through a basic alumina column to remove the radical inhibitor.

2.2 Instrumentation

Proton nuclear magnetic resonance (¹H-NMR) spectra were collected on a Bruker 500 MHz instrument. The ¹H-NMR spectra were referenced to signals from residual chloroform (7.26 ppm) in CDCl₃. The molecular weights (Mₙ and Mₘ) and polydispersity of the resulting block copolymers were determined using a Waters e2625 gel permeation
chromatography (GPC) with Waters 2414 refractive index detector (RI). The columns consisted of Styrage® (HR 3, HR 4 and HR 4E), and the GPC was operated at 30 °C using toluene with a 0.3 mL/min flow rate.

2.3 Synthesis of PVMS-b-PMMA

PVMS-b-PMMA was synthesized by first synthesizing the PMMA and PVMS homopolymers, and later chemically joining the homopolymers to make PVMS-b-PMMA. The preferred synthesis technique for preparing PMMA was by atom transfer radical polymerization (ATRP) and PVMS by anionic polymerization. Finally, the two end-functionalized homopolymers were conjoined by “click reaction”.

2.3.1 Synthesis of ω-Bromo-PVMS

THF (30 mL) was added into a 50 mL flame dried two-neck flask. VD3 (13 mL, 50 mmol) monomer was then charged into the reaction flask. n-BuLi (0.46 mL, 0.69 mmol) was added into the solution to initiate the reaction, and after 2 hours of stirring under argon, the reaction was quenched using 11-bromoundecyldimethylchlorosilane (0.43 mL, 1.38 mmol). The termination reaction was conducted by stirring the contents overnight in the sealed flask. Work-up involved dissolving the solution in n-hexane (50 mL) and washing three times with distilled water (30 mL) to remove salts from the lithium initiator. The organic material was then concentrated under vacuum to obtain a clear viscous liquid. PVMS was then precipitated out in methanol (30 mL). $^1$H-NMR results are shown in Figure 2-2 with the distinct peaks at 0.65, and 0.7, 3.4 ppm, which correspond to the end-group functionalized of the PVMS homopolymer. These peaks signify the end-functionalized silane terminating agent and n-BuLi initiator. $^1$H NMR (500 MHz, CDCl$_3$, δ):
6.06-5.92 (m, 1H, CH), 5.86-5.78 (m, 1H, CH₂), 3.48 (t, J = 7 Hz, 2H; CH₂), 1.93-1.85 (m, 2H Br-CH₂-CH₂), 1.48-1.4 (m, 2H, CH₃-(CH₂)₃-(PVMS)), 1.37-1.3 (m, 8H, CH₃-(CH₂)₃-(PVMS)-(CH₂)₉CH₂Br, 0.93-0.86 (t, J = 7 Hz CH₃-(CH₂)₃-(PVMS), 0.68-0.61 (m, 2H, Br-CH₂-(CH₂)₉-CH₂-PVMS), 0.58-0.49 (m, 2H, CH₃-(CH₂)₂CH₂(PVMS)), 0.21 to 0 (3H, PVMS backbone). GPC: Mₙ = 7,200 g/mol PDI = 1.2

2.3.2 Synthesis of ω-azido-PVMS

ω-Bromo-PVMS (2.5 g, 0.34 mmol), DMF (30 mL), DME (30 mL), and NaN₃ (270 mg, 4.2 mmol) were all added in a 25 mL flask. The reaction was carried out at ambient conditions and allowed to stir overnight. The final material was dissolved in n-hexane (50 mL) and washed three times with deionized water (30 mL). The organic phase was then concentrated in vacuum and dried under high-vacuum, and no further purification was needed. ¹H NMR (500 MHz, CDCl₃, δ): 6.06-5.92 (m, 1H, CH), 5.86-5.78 (m, 1H, CH₂), 3.28 (t, J = 7 Hz, 2H; CH₂), 1.67-1.6 (m, 2H Br-CH₂-CH₂), 1.44-1.2 (m, 8H, CH₃-(CH₂)₃-(PVMS), 1.37-1.3 (m, CH₃-(CH₂)₃-(PVMS)-(CH₂)₉CH₂Br, 0.94-0.86 (t, J = 7 Hz CH₃-(CH₂)₃-(PVMS), 0.68-0.61 (m, 2H, Br-CH₂-(CH₂)₉-CH₂-PVMS), 0.58-0.49 (m, 2H, CH₃-(CH₂)₂CH₂(PVMS)), 0.21 to 0 (3H, PVMS backbone).

2.3.3 Synthesis of α—propargyl-ωBromo-PMMA by ATRP

In a typical controlled radical polymerization for synthesizing PMMA, propargyl 2-bromoisobutyrate (50 mg, 0.24 mmol), PMDETA (13 mg, 0.073 mmol), Sn(EH)₂ (30 mg, 0.073 mmol), MMA monomer (3.6 g, 37 mmol), and anisole (5.4 g) were added into a two-
After two cycles of freeze/pump/thaw, Cu(I)Br (3 mg, 0.024 mmol) was added to the reaction flask. After a third freeze/pump/thaw cycle, the reaction mixture was warmed to room temperature before being placed into a preheated oil bath at 60 °C and allowed to stir under argon for 20 minutes. The reaction mixture was cooled to room temperature and purified by dissolving the final product in dichloromethane (60 mL) and washing any excess Cu(I)Br with aqueous ammonium chloride (NH₄Cl) (30 mL). This was followed by concentration in a vacuum, and subsequent precipitation into methanol to collect the polymer as a white solid. ¹H NMR (500 MHz, CDCl₃, δ): 4.68-4.64 (d, 1H, CH), 3.7-3.4 (s, 3H, CH₃), 2.1-0.65 (PMMA backbone). GPC: Mₙ = 4,100 g/mol, PDI = 1.23.

2.3.4 Synthesis of PVMS-b-PMMA

The previously synthesized ω-azido-PVMS (0.8g, 7.3*10⁻⁵ mmol, 1.1 eq.) and PMMA (0.64 g, 6.39*10⁻⁵ mmol, 1 eq.) were added in a reaction flask including PMDETA (0.19 g, 0.001*10⁻⁵ mmol, 15 eq.) and dichloromethane (40 mL). This was followed by three consecutive freeze/pump/thaw cycles on the flask. Finally, Cu(I)Br (0.157 g, 1.1 mmol, 15 eq.) was added while the argon was purging the flask, and then followed by an additional freeze/pump/thaw cycle. The reaction was stirred under argon for 24 hours. Analysis of the chain fidelity was performed by ¹H NMR and IR spectroscopy to confirm end-group functionalization from both starting materials and products, and successfully clicking the two polymers. ¹H NMR (500 MHz, CDCl₃, δ): 7.57 (s, 1H, triazole), 6.06-5.92 (m, 1H, CH), 5.86-5.78 (m, 1H, CH₂), 5.22-5.12 (m, 2H, -O-CH₂-triazole), 4.31 (s, 2H, PVMS-(CH₂)₂-triazole), 3.59 (s, PMMA) 2.23-0.05 (m, PMMA and PVMS). SEC: Mₙ = 9,500 PDI = 1.27.
2.4 Thin Film Preparation and Characterization

Silicon wafers (Nova Electronic Materials, <100>) were rinsed with toluene, cleaned with ultraviolet-ozone (UVO) cleaner (Jelight Model 42), and then rinsed with toluene prior to use. PVMS-b-PMMA was cast on the silicon substrate by spin coating from 1 wt% solution in dichloromethane at a spin speed of 3000 rpm for 45 s with acceleration at 300 rpm/s. In a separate vial with the same concentration of polymer, 2,2-dimethoxy-2-phenylacetophenone (DMPA), a radical initiator, was added to cross-link the film after solvent vapor annealing. Film thickness was measured using spectral reflectance (Filmetrics F20-UV) and determined to be 40 ± 5 nm. Reactive ion etching (RIE) was performed on thin film samples using a Phantom RIE by Trion Technology under CF₄ gas at 50 W for 5 seconds using 30 sccm, followed by oxygen plasma etching at 90 W for 60 seconds at 30 sccm.

Both thermal and solvent annealing was performed on multiple samples and the self-assembled morphologies analyzed. Thermal annealing was done by pre-annealing as cast films at 50 °C for 14 hours under vacuum to remove residual solvent from film casting, followed by increasing the temperature to 130 °C for 24 hours, while still under vacuum.

Solvent vapor annealing (SVA) was performed inside a glass chamber with an open flow system using a mixture of both acetone and heptane as solvents with N₂ carrier gas carrier to generate solvent vapor. Film thickness was continuously measured using spectral reflectance while swelling the film thickness. Additionally, the initial solvent
composition and final solvent composition were measured by collecting the vapor in dry ice-cooled contained and analyzed using $^1$H NMR (Table 2-1).

While still annealing, the sample was exposed under UV irradiation at a wavelength of 365 nm and intensity of 5 mW/cm$^2$ for 10 min. Previous in situ observations of solvent annealing showed that the degree of ordering reaches a maximum during the swelling state, however, during the deswelling stress imposed on the polymer resulted in disordering. Hence, UV exposure was used to lock in the optimum ordering and limit structural collapse during deswelling.

Morphological characterization was done using atomic force microscopy (AFM) (Bruker Dimension ICON) operating in tapping mode using commercially available Si tips (Budget sensors, 320 kHz). The tapping mode condition included a set point of $A/A_0 = 0.8$, where $A$ and $A_0$ are the ratio between the “tapping” mode amplitude set point and the free cantilever amplitude.

3. Results and discussion

3.1 Synthesis of PVMS-b-PMMA block copolymer

The successful synthesis of PVMS-b-PMMA was done using a combination of controlled polymerization and joining the final product via “click” reaction, other polymers using the same technique were made and listed in Table A-1. Figure 2-1 illustrates the synthetic methods used for obtaining the individual homopolymers, as well as the final block copolymer. ω-Bromo-PVMS was prepared by anionic polymerization of a VD3 monomer followed by end-group functionalization with 11-
bromoundecydimethylchlorosilane capping agent. Given the ease of reactivity with the tethered bromide end-group, this capping agent allows for future reactions. $^1$H-NMR was used to verify the end group functionalization with distinctive peaks being present at 3.4 ppm (a), and between 0.5-0.7 ppm (Figure 2-2, b and c peaks). The ratio of peaks a,b, and c are important in quantifying the amount of end group functionalization with current results showing 100% pendant fidelity. Earlier work by Kim et al. was instrumental in guiding peak assignments. The additional vinyl pendant group on the PVMS provides a strong doublet peak of 5.78 -6.1 ppm. The same bromide group on the ω-bromo-PVMS later was converted into an azide by SN$_2$ substitution under ambient conditions. This second reaction was done using a co-solvent because of PVMS solubility in non-polar solvents DME and the sodium azide being soluble in polar DMF solvent. The reaction was stirred overnight and immediately worked up in preparation for the “click” reaction. It should be noted that ω-azido-PVMS changed in color – clear to yellow - after storage for longer times under ambient conditions. Furthermore, GPC graphs showed broadening, which could indicate the degradation of the material (Figure 2-4). The vinyl azides have been demonstrated to be thermal- and photo-reactive, hence the need to “click” them immediately. We later referred to the $^1$H-NMR to confirm reaction progress. The chemical change from bromide to an azide should result in a slight shift in the location of the peak marked “a” to “a’” in Figure 2-2. With regards to the PMMA homopolymer, the alkynyl end-group (“d”) was identified to ensure end-group functionality (Figure 2-2).

Since the development of “click chemistry”, this conventional method has been exhaustively used in the pharmaceuticals, drug development, and polymers.
benefits of the copper(I)-catalyzed 1,2,3-triazole ring formation include a high degree of dependability, complete specificity, and high yields. The azide-alkyne Huisgen cycloaddition of the homopolymers was performed under argon to maximize CuI in order to facilitate the reaction. In preparation for the reaction, ω-azido-PVMS (10 mol%) was used in excess to ensure complete reaction with the PMMA. Upon reaction completion, the excess PVMS is easily removed by washing the polymer (1 g) in n-hexane (1 ml) given its high solubility in the solvent, while the block copolymer precipitates out. 1H-NMR spectrum was obtained of the final polymer confirmed the presence of specific functional groups related to the triazole ring formation. The proton located in the triazole group has distinct chemical shifts located at “e” on Figure 2-2 and comparing its peak area with adjacent groups (peaks “d’” and “a’”) reveal a ratio 1:2, which is expected given the number of protons present (Figure 2-2). Furthermore, the absence of the alkynyl end-group peak at ≈4.6 ppm revealed the absence of any PMMA homopolymer. GPC was used to study the reaction progress with the final block copolymer expected to have a larger molecular weight than the starting materials (Figure 2-3). The GPC spectrum shows narrowly dispersed homopolymers and block copolymer was synthesized, which was indicative of controlled polymerization techniques used. Additionally, narrowly distributed synthesized homopolymers are ideal given that the final block copolymer molecular weight and PDI is dependent on the homopolymer. The final “click reaction” product shows lack of any peak broadening in the GPC which confirmed complete reaction and lack of any unwanted side reactions. The final molecular weight does not equal a summation of the individual polymer chains given the very large difference in
hydrodynamic radius of the polymers in toluene during GPC. The polystyrene standards are incapable of predicting with great accuracy polymers with very different hydrodynamic radius. Finally, infrared spectroscopy was used to confirm any impurities from unreacted homopolymers. (Figure 2-4).

Figure 2-2 NMR of characterization of homopolymers ω-bromo-PVMS, ω-azido-PVMS, PMMA, and finally the BCP PVMS-b-PMMA.
Figure 2-3 GPC curves showing shift increase in molecular weight from “click” chemistry, with other peaks depicting homopolymers. The blue curve shows well-controlled PVMS-b-PMMA, the red curve showing PVMS homopolymer, and the yellow curve showing PVMS. The lack of peak broadening is an indication of complete “click” reaction without side reactions.
Figure 2-4 Infrared spectroscopy showing the starting precursor functional group and the “click” reaction product. The peak at $\approx 2100 \text{ cm}^{-1}$ is an azide peak from the PVMS homopolymer, which disappears after the two homopolymers are reacted to form the diblock copolymer without any presence of starting material in the final BCP at the bottom image.
Figure 2-5 Traces of PVMS post polymerizing after end-group functionalization with azide. The black line corresponds to PVMS after 2-day storage, while the black line is PVMS post GPC measurement on the same day as reaction ended.

3.2 Thin film studies

Self-assembly studies of the BCP were performed on silicon wafers with the goal of controlling orientation in thin films (10-100 nm). Thin films are especially interesting because factors such as film thickness, surface effects, and annealing processes can affect morphology and orientation. In our work, we studied both the impact of thermal and solvent annealing in thin films for developing nanostructure with sub-15 nm features, which have potential use in nanoporous membranes.
The films were thermally annealed at 130 °C for 24 hours under vacuum. Due to the large difference in surface energy between PVMS and PMMA (\(\gamma_{\text{PVMS}} \approx 20.5 \text{ mN/m}, \gamma_{\text{PMMA}} = 41.0 \text{ mN/m}\))\(^95\) coupled with the asymmetric volume fraction, the morphology was expected to form isotropic cylinders oriented in-plane to the substrate. The parallel cylinders are known to form due to preferential wetting of one block to both free-surface and substrate.\(^96\) The AFM image shows a PVMS matrix represented as a bright yellow surface, whereas PMMA is the minority material forming the dark lines (Figure 2-5a). It should be noted that prior to imaging, the films were etched by RIE to remove \(\approx 5 \text{ nm}\) of the PVMS wetting layer from the free surface formed during annealing.

Figure 2-6 AFM height images depicting the different morphologies from (a) thermally annealing PVMS-b-PMMA, (b) solvent annealing of PVMS-b-PMMA
Solvent annealing was employed to control the orientation of the thin films, while still maintaining the cylindrical morphology. A surface neutralizing bottom-coat of 40% poly(vinyl acetate) (40% hydrolyzed) was added for this treatment. The bottom-coat reduces the difference in interfacial energy between individual domains and the substrate ($\Delta \gamma_{\text{PVMS-substrate}} - \gamma_{\text{PMMA-substrate}}$), hence allowing for complete out-of-plane orientation. Furthermore, without surface treatment, PVMS tends to dewet from the silicon wafer making it difficult to spread the polymer evenly. To mitigate dewetting issues, PVA was used to improve the surface interaction between PVMS and the coated PVA silicon substrate.

Tuning of the morphology was employed by the dual solvent system of acetone/heptane. The acetone solubility parameter ($\delta$, 20 MPa$^{1/2}$) is similar to the PMMA solubility ($\delta$ 19 MPa$^{1/2}$) domain, hence preference towards it. Whereas, the solubility of heptane ($\delta = 15.3$ MPa$^{1/2}$) is preferential to the PVMS domain ($\delta \approx 15$ MPa$^{1/2}$). By tuning the vapor fraction during annealing, this can impact the swelling of individual domain spacing, which later results in changes in orientation, morphology, period length, and defects. The UV exposure is done in situ on films to lock-in the optimum ordering and limits structural collapse during deswelling. Additionally, cross-linking of the PVMS allows for mechanical tuning of the polymer by controlling the cross-linking density, with the possibility of attaining elastic moduli ranging from ~10kPa to ~1 MPa. In developing porous features of sub-10 nm, we are the first to show work based on a silicon-based block copolymer with ease of etching, while still maintaining PVMS functionality for future post-modification.
During the SVA experiments, we experimented with several different solvent compositions of acetone and heptane to understand the impact on the final morphology (Figure 2-7). Prior work by Jung and Ross\textsuperscript{98} showed that solvent vapor composition can be an effective tool to engineer and control morphology and orientation. In following this work, we show the effect of mixed solvent composition on the ordering and orientation of the film. Initially, pure acetone was used to swell the films with the aim of propagating the PMMA towards the free-surface, however, the final morphology observed tended to favor parallel cylinder. The large difference in solubility parameter between acetone and PVMS ($|\delta_{\text{acetone}} d| - \delta_{\text{PVMS}} | \approx | 20 \text{ MPa}^{1/2} - 15 \text{ MPa}^{1/2} | j= 5 \text{ MPa}^{1/2}$) leads to more swelling in the PMMA. The more swelling in PMMA results in a reduction in surface energy that follows with the movement towards the free surface. In having an already mobile polymer - PVMS – the still differing surface energies and mobility of the chains still result in several defects, poorly ordered domain spacing, orientation, and morphology. Hence, the films that were exposed to acetone vapor only presented parallel cylinders and as we progressively increased the volume composition to include heptane, we gradual show a shift in defects and orientation. The explanation for the improved orientation is brought by the changing of the surface energies to cater to surface neutralization, which allows for perpendicular orientation. The desired perpendicular orientation was achieved by selecting a solvent composition with both acetone and heptane volume fraction being close to each other (79 vol\% acetone) (Table 2-1).
Figure 2-7 AFM images showing the morphological variation of PVMS-b-PMMA using a film swelling ratio (S.R.) of 1.15. As the solvent composition changes the morphology shifts from a poorly ordered morphology compromising of mostly parallel cylinders with only acetone (100 vol. %) to uniform perpendicular structure using a solvent composition of acetone/heptane (75:25 vol. %)
Table 2-2 Solvent collection measurements during solvent annealing

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<th>Acetone (vol%)</th>
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Figure 2-8 Impact of the swelling ratio of the films during SVA using a solvent composition of acetone to heptane 55:45 vol%. using a) 1.15 b) 1.3 c) 1.7. Table 2-1 can be used as a reference for vapor composition.

We also explored the impact of the swelling ratio (Film thickness during swelling/Initial film thickness) on the self-assembly of the BCP (Figure 2-8). In our system given that we are dealing with films ≈2.5 L₀ (40 nm), we investigated the impact of swelling ratio on the final morphology. While solvent annealing at various swelling ratios (SR) we observed a shift in morphology from perpendicular cylinders to mushroom morphology. Prior work by Gong et al.¹⁰¹ revealed unique mushroom-shaped features presented during the solvent annealing with acetone. We hypothesize that at high SR, more acetone is absorbed in the film due to its high vapor content, and this is compensated by over-
swelling of the PMMA domain spacing as it moves towards the free-surface. Finally, during the deswelling stage, a rapid shrinkage of PMMA domain results in a depressed PMMA continuous phases at the film surfaces. And, this was observed with the increase in defects and poor order from increasing swelling ratio for 1.15 to 1.7.

Figure 2-9 100 nm film thickness showed mixed morphology through film, but line cut showed domain spacing 13 nm (a) AFM height image (b) AFM morphological phase image (c) GISAXS scattering

Grazing incidence small-angle X-ray (GISAXS) showed poor ordering with an arc formation indicating a mixture of both parallel and perpendicular morphology (Figure 2-9). The feature size measure was calculated to be 13 nm. However, due to the poor structure, utilized in situ cross-linking of the film immediately after the solvent annealing
time to freeze the morphology and prevent reverting the structure during deswelling. However, we were not able to collect GISAXS images after cross-linking the film. Additionally, we reduced the operating film from 100 nm to 40 nm to prevent morphological defects due to thicker films. The topography of bulk films was additionally looked at by transmission electron microscopy (TEM) and we observed cylindrical holes in the film indicative of perpendicular cylinders through the film.

4. Conclusion

Self-assembly of block copolymers (BCPs) is quintessential to various applications whereby small feature sizes are required, such as nano-electronics and membranes. In using silicone-based copolymers, the aim was to exploit high $\chi$ interactions between individual blocks to obtain a patterned structure with very small feature sizes. PVMS-b-PMMA was synthesized as an ideal precursor for the porous films. The synthesis was performed using both anionic and atom transfer radical polymerization, as well as “click” chemistry. To achieve the desired orthogonal cylindrical structure, we utilized a combination of both solvent vapor annealing and top-coat as a surface-neutralizing technique.
Chapter 3: Efficient synthesis of cyclic PVMS-b-PMMA

Cyclic block copolymers are of great interest due to new properties resulting from the unconventional polymeric architecture. In trying to further understand the material, we designed a synthesis scheme for making cyclic poly(vinylmethysiloxane-block-methylmethacrylate) (c-PVMS-b-PMMA) polymer keeping in mind the challenges regarding end-group functionality and purity. This chapter describes work done on the synthesis of c-PVMS-b-PMMA and PVMS-b-PMMA-b-PMMA or PVMS-b-PMMA-b-PVMS triblock copolymers. The underlying work aims at understanding (1) efficient synthesis conditions to provide high purity and yield, and (2) end-group characterization of homopolymers.

1. Introduction

Cyclic block copolymers (BCPs) present an appealing class of block copolymers given their unique topology. The topology consists of a defect-free linear analogous with the chain ends chemically bound together. The absence of end-groups has resulted in a great contribution of diffusion and conformation in comparison with the linear analog,\textsuperscript{102} leading to new material properties. Some of the reported changes in physical properties include increased glass transition temperatures ($T_\text{g}$), melting temperature ($T_\text{m}$), crystal morphology, melt viscosity, and smaller hydrodynamic volumes.\textsuperscript{102-103} For example, the glass transition temperature of polymers occurs when the configuration entropy reaches
a critically small value. Due to cyclic polymers having a fewer number of configurations, this results in a higher glass transition temperature.\textsuperscript{104} Apart from having higher glass transition temperature, the $T_g$ of cyclic polymers has a weaker molecular weight dependence due to the absence of chain ends and relatively low configurational entropy.\textsuperscript{105}

In the block copolymer field, the cyclic topology is developing great interest given the efficient packing which results in smaller characteristic lengths upon phase separation in comparison to linear BCPs. Poelma et al.\textsuperscript{24b} showed a reduction of about 33\% in features sizes as a result of the ring closure of a linear analog. This work is especially relevant due to the growing demand for smaller lithographic templates in the microelectronics industry.\textsuperscript{83} Additionally, limitations towards reducing the total molecular weight to achieve the smaller characteristic lengths are of interest in the polymeric field. The cyclic BCPs conforms into a double-looped structure. This involves both polymer blocks forming a loop in their respective domains and the two junction points between the blocks reside at the interface resulting in a smaller feature size in comparison to linear BCPs.\textsuperscript{26} The linear BCP analog conforms to a bridge assembly - which involves both chains end in their respective domains.\textsuperscript{27}

As noted from the new properties from cyclic polymers, precise control of the polymer architecture has attracted the attention of several polymer scientists. The greatest challenge to the chemist has been to synthesize cyclic polymers in high yield and greater purity. Currently, there are two popular methods of producing macrocyclic by either ring-closure or ring expansion.\textsuperscript{103, 106} The ring-closure technique is especially
relevant when making block copolymers. The requirements are ultrahigh dilution to favor either unimolecular or bimolecular cyclization. Because of the very high dilution, the reaction is usually limited to a very small scale (5-100 mg) and also a limited to $M_n$ of approximately 25,000 g/mol as a consequence of the entropic penalties associated with localizing the two chain ends, close enough into a region of space to allow for intramolecular coupling of chain ends.$^{103}$ The magnitude of difficulty in synthesizing cyclic BCPs is heightened especially when performing bimolecular ring closure. In this procedure, stoichiometric amounts of homopolymers must be present to prevent impurities. Despite the limitation with stoichiometric ratios and ultra-dilution, biomolecular cyclization is an ideal method to develop BCPs whose constituent blocks are incompatible polymers requiring synthesis by different polymerization techniques.

In this chapter, we focus on tackling and developing an efficient method of using a combination of click chemistry to combine two otherwise unlikely cojoined homopolymers into forming a novel cyclic block copolymer. The primary interest of our works is guided by the small domain spacings achievable in cyclic BCPs created from highly incompatible homopolymers.
Figure 3-1 Synthesis of c-PVMS-b-PMMA from linear difunctional homopolymers α,ω-diazido-PVMS α,ω-bromo-PMMA. In the earliest reaction α,ω-diazido-PVMS made using a combination of anionic and end-group substitution. α,ω-bromo-PMMA was created using ATRP and end-group substitution. Finally, c-PVMS-b-PMMA using “click chemistry”

2. Materials & Methods

2.1 Materials

All reagents were used as received from chemical vendors unless otherwise noted. Tetrahydrofuran (THF) which was dried with a solvent purifying system from Mbraun (MB-SPS-800). 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (VD3) was purchased from Gelest. The following reagents were purchased from Sigma-Aldrich: n-butyl lithium solution in hexane (2.5 M), sodium azide (NaN₃), propargylamine, 2-Bromo-2-methylpropionyl bromide, dimethylformamide (DMF), dimethoxyethane (DME),
diphenylsilanediol, propargyl-2-bromoisobutyrate, N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA), sodium bicarbonate, ethylenediaminetetraacetic acid, copper (I) bromide (Cu(I)Br), methyl methacrylate (MMA), and tin (II) 2-ethylhexanoate (Sn(EH)₂). Other solvents including methanol were sourced from EMD Millipore and dichloromethane from BDH was used. Prior to performing synthesis, the monomer VD3 was freeze/pump/thaw 3 times with argon and dried overnight on molecular sieves; while MMA was run through a basic alumina column to remove radical inhibitor.

2.2 Instrumentation

Nuclear magnetic resonance (NMR) spectra’s were collected on a Bruker 500 MHz instrument. The ¹H NMR spectra were referenced to signals from residual chloroform (7.26 ppm) in CDCl₃. The molecular weights (Mₙ and Mₘ) and polydispersity of the resulting block copolymers were determined using a Waters e2625 gel permeation chromatography (GPC) with Waters 2414 refractive index detector (RI). The columns consisted of Styrage® (HR 3, HR 4 and HR 4E), and the GPC was operating at 30 °C with toluene solvent flowing at 0.3 ml/min flow rate. For the cyclic BCPs with impurities, the polymers were run through prep-GPC to remove impurities. The polarity of the RI detector must be switched to negative (-) when running PVMS and PVMS-b-PMMA; whereas for PMMA the polarity should be positive (+).

The mass spectrometric analysis was performed using a Bruker AutoflexIII MALDI-TOF mass spectrometer (Bruker Daltonics, Billerica, MA). Data were acquired using
reflector-positive ion mode, with an acceleration voltage of 20 kV, and delayed extraction. Data acquisition was performed using Bruker Daltonics flexControl 3.0 software and data analysis was carried out with Bruker Daltonics FlexAnalysis 3.0 software.  

For PMMA homopolymers, α-cyano-4-hydroxycinnamic acid was used as the matrix and sodium trifluoroacetate was the cation source. Both the polymer and the counterion solutions had a concentration of 10 mg/mL. The concentration of the matrix solution was 30 mg/mL. The same ingredients and concentrations were used for PVMS except the matrix used was dithranol.

2.3 Synthesis of cyclic PVMS-b-PMMA block copolymer

c-PVMS-b-PMMA was made by first independently synthesizing both individual PMMA and PVMS, and finally cyclizing the bi-functionalized linear homopolymers under highly dilute conditions to form a block copolymer. The preferred synthesis technique for preparing poly(vinylmethyldimethylsiloxane) (PVMS) was anionic polymerization and poly(methyl methacrylate) (PMMA) was made by atom transfer radical polymerization (ATRP). Both polymerization techniques involved initiating with a bifunctional initiator. As a result of both homopolymers having reactive end-groups, the final cyclic block copolymer can be made by “clicking” the individual homopolymers together.

2.3.1 Synthesis of α,ω-dibromo-PVMS

The anionic polymerization initiator, diphenylsilanolate (0.32 g, 1.5 mmol) was added into a 250 mL two-neck flask and a high vacuum pulled to evacuate the air. This was followed by using a flame torch to heat the sides of the glassware removing any moisture. The vacuum was released by purging with argon and the procedure repeated.
two more times. After that, THF (30 mL), that was dried the prior night with molecular sieves was injected into the flask. The reaction flask was then cooled with dry ice before adding n-butyl lithium (1.38 g, 3 mmol) drop-wise into the flask, while the flask was continuously stirred under argon. After 15 minutes of stirring, VD3 monomer was syringed into the reaction flask and the dry ice bath removed to allow the reaction to progress at room temperature for 30 minutes. The anionic reaction was terminated using glacial acetic acid (10 vol% in methanol). Work-up involved dissolving the solution in n-hexane (50 mL) and washing with sodium bicarbonate (aq.) to neutralize the solution. The organic material was then concentrated under vacuum to obtain a clear viscous liquid. PVMS was then precipitated in methanol (30 mL). GPC: Mn = 8,500 g/mol PDI = 1.36

2.3.2 Synthesis of α,ω-diazido-PVMS

In a 25-mL flask α,ω-dibromo-PVMS (2.5 g, 0.31 mmol), DMF (10 mL), DME (10 mL) and NaN₃ (270 mg, 4.2 mmol) were all added. The reaction proceeded at ambient condition and was stirred overnight. The final material was dissolved in n-hexane (50 mL) and washed three times with deionized water (30 mL). The organic phase was then concentrated under high vacuum and dried overnight under high-vacuum, and no further purification was undertaken.

2.3.3 Synthesis of α,ω-bromo-PMMA by ATRP

In a typical controlled radical polymerization for obtaining PMMA, ethylene bis(2-bromoisobutyrate (50 mg, 0.24 mmol), PMDETA (13 mg, 0.073 mmol), Sn(EH)₂ (30 mg, 0.073 mmol), MMA monomer (3.6 g, 37 mmol) and anisole (4.7 g) were added into a two-neck 50 mL round-bottom flask. After two cycles of freeze/pump/thaw, Cu(I)Br (3 mg,
0.024 mmol) was added to the reaction flask. After the third freeze/pump/thaw cycle, the reaction mixture was warmed to room temperature before being placed into a preheated oil bath at 60 °C and allowed to stir under argon for 1 hour. The reaction mixture was cooled to room temperature and purified by dissolving the final product in dichloromethane (60 mL) and washing off Cu(I)Br with aqueous ammonium chloride (NH₄Cl) (30 mL). This was followed by concentration in a vacuum, and later precipitating into methanol to collect polymer as a white solid. GPC: $M_n = 8,700$ g/mol PDI = 1.3

2.3.4 Synthesis of $\alpha, \omega$-propargyl-PMMA

In a 250 mL flask DMF (5 mL), PMMA (0.5 gm, 0.057 mmol), triethylamine (24 mg, 0.18 mmol) and propargylamide (10 mg, 0.18 mmol) were added. The reaction flask was heated to 40 °C overnight for reaction completion. Work up involved precipitating the product in water to obtain a white product, then dissolving the product in dichloromethane, and re-precipitating. The polymer color changed from yellow to white once residual propargylamine was washed out. $M_n = 8,700$ g/mol PDI = 1.3

2.3.5 Synthesis of cyclic PVMS-b-PMMA

The cyclic block copolymer was synthesized by intermolecular “click” coupling reaction of both linear telechelic alkyne and azide functionalized homopolymers. In a 500 ml flask dichloromethane (330 mL), PMDETA (129 mg, 0.74 mmol), SnEH₂ (302 mg, 0.74) were added the flask and underwent 2 freeze/pump/thaw cycles before Cu(I)Br (2.6 mg, 0.0187 mg) was added. Using a second flask, the bifunctional homopolymers – PMMA (31 mg, 0.0037 mmol) and PVMS (28 mg, 0.0037) and dichloromethane (10 mL) - were all added and underwent 3 freezes/pump/thaw cycles. The solution in the polymer flask was
then withdrawn with a 25 mL syringe and placed on a syringe pump with a flow rate of 0.3 mL/hr. To minimize the intermolecular reactions and favor the ring closure, the cyclization was run at very low concentration with the polymer injection rate being 1.76 mg/hr during the whole reaction time. After the syringe had completed injecting all the contents, the flask with the polymeric contents was stirred for an extra day before work up. Work up involved dissolving the final product in dichloromethane (10 mL) and washing off Cu(I)Br with aqueous ethylenediaminetetraacetic acid (aq., 30 mL) three times. GPC: $M_n = 15,800$ g/mol PDI = 1.18

3. Results and discussion

Cyclic PVMS-b-PMMA was successfully synthesized using a combination of ATRP, anionic polymerization, and “click chemistry”. The cyclization was possible because of (1) high dilution conditions and (2) high end-group fidelity in the homopolymers. The high dilution ring-closure is an effective method of mitigating any undesired linear block copolymers, however, cyclization is still limited by molecular weight.\textsuperscript{24b, 109} In synthesizing the polymer, GPC, $^1$H NMR, and MALDI were quintessential in observing the reaction progress.
Figure 3-2 NMR characterization of homopolymers (a) α,ω-dihydroxy-PVMS, (b) α,ω-dibromo-PVMS (c) α,ω-azido-PVMS , (d) α,ω-dibromo-PMMA, (e) α,ω-propargyl-PMMA (f) cyclic PVMS-b-PMMA

NMR provides insightful information about the bond formation and end-group functionalization. During the anionic polymerization, the initiation is expected to occur from the diphenylsilanediol anion. The aromatic backbone in the diphenylsilanediol is well characterized with signature peaks formation approximated 7.25-7.6 ppm located next to the chloroform solvent (Figure 3-2). Additionally, we confirmed that the reaction was completely initiated by a diphenylsilanediol instead of n-butyl lithium by comparing NMR
spectrum between the bifunctional PVMS polymer, and a previously synthesized monofunctional PVMS using n-butyl lithium (Figure 3-3). The lack of any distinctive n-butyl lithium peaks ≈ 0.6 ppm allowed us to proceed to the next reaction steps with confidence that the polymerization was initiated only from diphenylsilanediol anions and not from residual n-butyllithium. The PMMA was synthesized by ARGET-ATRP which has been shown to have over 90% end-group functionality.\textsuperscript{54} The final polymer retains bromide groups on the chain end after successful polymerization that are susceptible to end-group conversion. Prior work by Cossen et al.\textsuperscript{110} successfully showed the end-group conversion of bromide groups to an amine by a simple substitution reaction without any side reaction.\textsuperscript{54} After the reaction, we observed new bond formation from the alkyne functional group at 2.3 ppm labeled “f” in Figure 3-2. Moreover, we characterize the alkyne peak both before and after converting the PMMA end-groups. IR spectra revealed the presence of the alkyne group at peak position ≈ 3300 cm\(^{-1}\) (Figure 3-6).

The complete characterization of the homopolymers was important before proceeding to the targeted cyclic BCP. In synthesizing the cyclic BCP, the formation of a triazole functional group is evident from the signature peak at ≈ 8.05 ppm.\textsuperscript{24b, 111} Additionally, the propargylamine has an adjacent proton on the ethyl group submerged under the PMMA peak at ≈ 3.5 ppm. However, after the reaction, the same protons are bounded to a more rigid amine group that results in de-shielding in the material with peak formation at 4.7 ppm labeled “g” in Figure 3-2. Additionally, the triazole bond forms at 8.1 ppm (“h”) and the ratio between triazole and ethyl on propargyl amine should be 2, as shown on the NMR. Further evidence of lack of triblock formation, we observe that the
molar compositions are relatively close to a 50:50 vol.% (peak ratio of “a” vs “c”), unlike with a triblock, where one polymer’s composition would be double the other.

In the synthesis of BCPs, a reduction in elution time and narrowness of the peak distribution is ideally important in justifying both reaction completion and purity. The GPC results from our experiments involving both the individual homopolymers shows monodisperse peaks which are indicative of the controlled ATRP and anionic polymerization (Figure 3-3).\textsuperscript{49, 112} The PMMA had a narrower distribution compared to PVMS and that was due to the robustness of ATRP to occur in humid conditions in comparison to early termination of anionic polymerization. The “click” reaction of the PVMS and PMMA end-functionalized homopolymers resulted in a narrowly distributed polymer; however, we did observe linear impurities according to the IR spectroscopy (Figure 3-7) at higher concentration (0.25 mg/mL) in comparison to lower concentration (0.08 mg/mL).
Figure 3-3 SEC graphs showing shift increase in molecular weight from “click” chemistry, with other peaks depicting homopolymers. The green curve shows well-controlled PVMS-b-PMMA, the red curve showing PVMS homopolymer, and the blue curve showing PMMA.

Apart from NMR, we also referred to Fourier transform infrared (FTIR) spectroscopy for any azide present in the final polymer. Evidence of complete reaction would be observed with complete disappearance of the azide peak in the IR spectrum at ≈ 2100 cm⁻¹ (Figure 3-4). However, before obtaining the pure cyclic block copolymer, residual impurities from unconverted linear homopolymers with azide groups needed to be removed. By performing prep-GPC on the material, we can extract a clean cyclic BCP with almost no presence of linear azide impurities. This was done by collecting 2 fractions with the knowledge that linear impurities have a larger hydrodynamic radius, hence will
be present at early detection times. This will correspond to the region of slight tailing at the beginning of the GPC curve. We collected two quantities from the prep-GPC with the first fraction collected upon first seeing any detection from the refractive index detector till the end of the forward tailing. The second fraction collected immediately upon ending collection of fraction 1 till the peak detection ended.

![Infrared spectra of the synthesis of c-PVMS-b-PMMA, linear PVMS homopolymer and crude c-PVMS-b-PMMA with azide impurities from linear chains. The linear impurities are identified from the azide peak at 2100 cm\(^{-1}\).](image)

The synthesis of cyclic block copolymers is possible only at high dilution to promote intramolecular reactions of the end-group; while suppressing any intermolecular
“clicking” of different polymer chains. Polymeropoulos et al.\textsuperscript{109a} were able to establish an ideal concentration of 0.2 mg/mL as the lowest concentration possible to develop high amounts of the cyclic block copolymer. In using the Glaser coupling reaction to conjoin the tailored same end-groups in unimolecular cyclization, they were able to synthesize successfully triblock copolymers at the high molecular weight. Additionally, Poelma et al.\textsuperscript{24b} were able to synthesize cyclic block copolymers using a bimolecular cyclization at a lower concentration of 0.125 mg/mL. Bimolecular cyclization presents several challenges regarding (1) exact stoichiometric ratios of homopolymer (2) high-end group efficacy (3) high probability of bimolecular reaction. To try and elucidate the correct concentration for the biomolecular cyclization two concentrations were selected. One of the concentrations was more than half the concentration used by Polymeropoulos et al.\textsuperscript{109a} (0.2 mg/mL), and the second concentration was slightly higher. Using the IR, the presence of azide peak provide evidence of linear impurities of azide (≈2100 cm\textsuperscript{-1}) present for high concentration; whereas the lower concentration presented no impurities (Figure 3-7).
Figure 3-5 NMR comparison between (a) n-butyl lithium initiated PVMS and (b) diphenylsilanediol initiated PVMS using anionic polymerization. The highlighted green region shows that VD3 initiation by n-butyl lithium results in two distinctive peaks, while initiation by diphenylsilanediol results in no peak.
Figure 3-6 Infrared spectra of end-group functionalized PMMA
Figure 3-7 IR spectra showing the effect of using a highly dilute (0.08 mg/ml) polymer concentration vs a more concentrate reaction solution. The presence of azide is indicative of either excess of one homopolymer or linear triblock homopolymer.

In addition to infrared spectroscopy, MALDI spectra were collected to compare the shift in mass from bromide to an alkyne end-functionalized polymer (Figure 3-8). The difference in molar mass between the bromide and alkyne functionalized homopolymers ($M_{nB}-M_{nprop} = 49$ Da) was used to further justify a complete reaction and high chain functionality between the starting material and product.
Figure 3-8 MALDI representation of PMMA before and after end-group conversion with bromide groups being present before and converted into amine groups with a change in relative Mn of 49 Da

4. Conclusion

The successful synthesis of a cyclic block copolymer was conducted by using “click” chemistry to bring otherwise very incompatible polymers. This synthesis approach provides a widely applicable approach to synthesizing silicon-containing cyclic BCPs. Effective characterization at each step to determine the presence of end-groups and appropriate conversion was needed to ensure reaction occurred at high yield. The purity of the final polymer was possible due to separation by prep-GPC and full characterization of the cyclic product by GPC, NMR, and IR.
Chapter 4: Development of hydrophobic coating on the microporous membrane for water-in-oil separation

Filtration membranes have been utilized in several water/oil separation processes with the primary emphasis on collecting water, while the oil is prevented from permeating through the membrane. Despite numerous applications using this gravity separation method, several challenges present themselves, especially when dealing with surfactants. Fouling of the membrane is the biggest challenge by inhibiting flow and limiting selectivity. To counter this, we reverse our membrane to allow the oil to permeate through instead of water. Additionally, we use poly(vinylmethylsiloxane) a known polymer to have antifouling properties to purify water-in-oil emulsions stabilized by Span 80 (emulsifier). This chapter focuses on the progress made using poly(vinylmethylsiloxane) as an effective anti-coating agent.

1. Introduction

The ever-growing demand to satisfy the energy consumption of the world has resulted in the expansion of exploration and drilling of oil. An increase in overall oil production has been welcomed due to the economic benefits coming along with increased employment; however, we are beginning to observe the consequence with several accidental spills and contamination of clean water in our local communities. The Deepwater Horizon explosion off the coast of Louisiana resulted in more than 210 million gallons of oil spewed into the ocean. This led to irreversible destruction of several aquatic species population and contamination of water streams. As a result of the number
of oil spills increasing, there is an ever-growing spotlight on preventing spills and efficient and economical methods of remediating oil-water mixtures.\textsuperscript{115}

Several techniques have been utilized to separate water-in-oil emulsions such as gravity separation, skimming, and flotation. For example skimming is probably the most commonly used technique, however, limitations such as low efficiency prevent full implementation of this method as standard ways of separating water-in-oil mixtures. Additionally, the water-in-oil mixture tends to form an emulsion, and with recent advances in hydraulic fracturing, the use of emulsifiers result in great difficulty in separation the water-in-oil emulsion.\textsuperscript{116} Hence, membrane technology has been observed as a viable technique to separate water-in-oil nano and micro-emulsions.\textsuperscript{80, 117} Porous membranes effectively satisfy the need for selectivity, high-throughput, and continuous use.\textsuperscript{118} The operation conditions will dictate the type of membrane with superhydrophobic/oleophilic or hydrophilic/oleophobic materials being selectively chosen for water-in-oil separation due to the lack of fouling.\textsuperscript{119}

The chemical composition of the surface impacts the hydrophobicity/hydrophilicity of a material. Low surface energy materials such as perfluorocarbon,\textsuperscript{117a} fluoroalkyl silane,\textsuperscript{120} and polymer coatings have been employed due to their superhydrophobicity.\textsuperscript{121} Fluorinated coating is a rudimentary method of converting a surface from hydrophilic to hydrophobic. However, due to the very low surface energy of a monolayer substance, this can also result in an oleophobic surface formation. Teflon®, a derivative of polytetrafluoroethylene, is a common fluorinated material with a low-adhesive surface, which has been shown to repel both organic and
aqueous materials. During the separation of water-in-oil, fouling is of great concern and to circumvent this scenario from occurring, a growing interest has moved toward hydrophobic/oleophilic surfaces. Other than fluorinated compounds, surface covered with a self-assembled monolayer of n-dodecanethiol is seen as a viable alternative to showcase both hydrophobicity/oleophilicity. Zhang et al. employed n-dodecane on a gold deposited surface, which had the added benefit of increased roughness on the surface. The monolayer induced super-hydrophobicity on the surface because of the aliphatic backbone. The main limitation of this method on an industrial scale is the cost of gold. This allows for the opportunity to develop a hydrophobic material effective enough to separate water-in-oil emulsion, while still being available at low cost.

Poly(vinylmethylsiloxane) (PVMS) is a silicon-based polymer that can be readily chemically-functionalized, which could encompass attaching hydrophobic and/or hydrophilic monolayer. Thiol-ene chemistry allows for effective functionalizing the vinyl-group on the PVMS. The low surface energy of the polymer is a result of the aliphatic groups on the side-group. The flexible polymer backbone can then allow for the low surface energy hydrocarbon groups on the side chains to be present at the free-surface, hence allowing the polymer to have hydrophobic properties. Also, unlike most toxic hydrophobic surfaces such as fluoropolymers, silicon-based materials present ease of use in mild and environmentally friendly use. In selecting PVMS for coating various membranes, we aim at understanding the impact of pore size on the separation of the oil-water mixture and allow the effectiveness in the surface to prevent permanent desorption of surfactant that can result in fouling.
2. Experimental

2.1 Materials

All reagents were used as received from chemical vendors unless otherwise noted.

From Sigma-Aldrich, the chemical purchased are ACS reagent grade decane, ACS reagent grade toluene azobisisobutyronitrile (AIBN), and Durapore PVDF membrane (GVHP04700 and DVPP04700). The cellulose filter paper (47 mm i.d.) was purchased from VWR.

Prior to performing synthesis, the monomer VD3 was freeze/pump/thaw 3 times with argon and dried overnight on molecular sieves. This is the exact method of synthesizing as chapter 2

2.2 Preparation of superhydrophobic membrane

A solution of PVMS (300 mg) in dichloromethane (10 mL) was continuously stirred before AIBN (20 mg) was added into the vial. The contents were poured into a petri dish and the individual support membranes were dip coated inside and then inserted into a vacuum oven at 130 °C for 1 hour to allow for crosslinking to occur. After that, the films were thoroughly washed with dichloromethane and allowed to dry before contact angle experiments were done to confirm an increase in contact angle for the cellulose and hydrophilic PVDF membrane.

2.3 Preparation of water-in-oil emulsion

Two kinds of surfactant-stabilized water-in-oil emulsions were made. The preparation involved adding water (20 mL) in toluene (180 mL) with Span 80 being 15 wt% of the water phase. The emulsion was stirred using a high shear mixer for 1 hour for
complete emulsification. The same preparation conditions were used for decane emulsions.

2.4 Vacuum filtration setup

The prepared superhydrophobic-superoleophillic membranes were placed in a vertical fritted vacuum filter of diameter 47 mm. The emulsions were then poured through the membrane with a controlled vacuum of 970 mbar to speed up the rate of flow. The experiments were conducted for a fixed 20 minutes and repeated 5 times. After each repeat, the membrane was rinsed with the organic solvent used for the water/oil emulsion. It was noted that during the experiment, phase separation occurred in the emulsified test solution over time, and this resulted in two-separate layers forming with water being present at the bottom layer and a separate water/decane emulsion being present above. The phenomena are known as creaming, which occurs when emulsions begin coalescing due to emulsion instability. Creaming hindered the flow of the emulsion through the membrane during the experiments.

2.3 Characterization

Scanning electron microscopy (SEM) was used to study morphology, size, and distribution of the PVDF membrane support using a Hitachi 4800 model. The goniometer was employed to quantify the contact angles, which allows us to understand the nature of surface hydrophobicity. All measurements were performed by using 5 μL of deionized water. The percentage purity was calculated using $^1$H-NMR (500 MHz) by Bruker using deuterated acetone, with the relative water/toluene or water/decane intensity peaks being integrated to find the quantity present of each amount after purification.
3. Results and Discussion

3.1 Emulsion droplet characterization

Emulsified oil, which consists of droplets of water with a diameter less than 150 μm is difficult to separate with conventional separation techniques such as gravity separation and skimmers. The introduction of surfactants into water-in-oil mixtures usually results in several other consequences from irreversible fouling on the membrane wall to poor selectivity in microporous structures. In the applied experiments we employ Span 80 (hydrophile-lipophile balance number, HLB = 4.3), as an emulsifier to stabilize water droplets in the oil phase. After vigorously mixing with a homogenizer, a uniform white emulsion for both water/toluene and water/decane is obtained (Figure 4-1). By retaining nanoemulsions, we aim at testing the efficiency of separating water/oil emulsion in the nanodroplets using microporous supports of different morphology and pore sizes. Peng et al. were able to effectively filter through non-surfactant stabilized water-in-oil mixtures using microporous membranes with high separation efficiency using a melanine sponge. The melanine sponge is a practical method of absorbing oil spills; however, an effective study of the impact of morphology and antifouling properties using a surfactant stabilized oil/water emulsion is required to furthering the oil remediation process.
Figure 4-1 Optical image of the surfactant-stabilized a) water-in-toluene emulsion b) water-in-decane emulsion. The other images include water-in-oil emulsion mixtures in their respective containers for c) water-in-toluene and d) water-in-decane emulsions

3.2 Membrane characterization

FE-SEM images of the membranes are shown in Figure 4-2. They reveal non-uniform and randomly oriented microporous structures (<2 μm) for the PVDF membranes; while the cellulose membrane has larger fibrous openings larger than 100 μm. The cellulose membrane had several fibrous structures on the surface, and this served as an important baseline into the argument of the impact of pore size on selectivity. The systematic development of membranes requires an optimum surface
porosity to help negate issues regarding selection but still allow high enough permeation.\textsuperscript{65} PVDF-650 and Cellulose were initially hydrophilic with water contact angle <1°; however, upon dip coating we observe an increase in hydrophobicity of the surface to 135°. PVDF-200 was already hydrophobic (c.a. 120 °); however, it showed a poor separation of water-in-oil emulsions and was later coated with the PVMS as an antifouling coating. The poor flux in PVDF-200 is attributed to PVDF being fouled with the surfactant and this impedes mobility or separation.\textsuperscript{128} Young’s model predicts that a surface retains both hydrophobicity and oleophillicity when the surface tension is between that of water (72.3 mN-m\textsuperscript{-1}) and oil (20-40 mN-m\textsuperscript{-1}).\textsuperscript{114,129} In selecting PVMS as the coating material we achieve (1) increased hydrophobicity with large contact angles (c.a. >130 °); (2) improved oleophillicity with the surface energy being 20.5 mNm\textsuperscript{-1}; and (3) maintenance of antifouling properties.\textsuperscript{130}
Figure 4-2 SEM images of PVMS coated membrane a) PVDF-200 b) PVDF-650 c) Cellulose

3.3 Membrane emulsion separation efficiency

Water-in-oil emulsions are stabilized by several surfactants such as asphaltene and natural surfactants present in crude oil. Asphaltenes and several of the surfactants non-ionic and result in water being emulsified during exploration. Despite several purification steps, residual water will remain present in the extracted oil. The water is emulsified into small droplets that are unable to be separated by physical filtration. De-emulsification with surfactants result in the introduction of a hazardous chemical into the environment, hence the need to develop a more efficient method is required.

Separation of the oil-in-way mixtures was conducted with a gravity-based filtration system. This system was selected due to the simplicity of implementation in the
lab. All the membranes were prior coated with PVMS coating to enhance hydrophobicity. The toluene solvent after filtration had over 98% purity for PVDF-200 and PVDF-650, however, it failed to achieve similar quantities with the cellulose membrane. The composition of filtrate from the cellulose was barely an improvement from the feed concentration (Figure 4-3). De-emulsification occurs when the membrane surface strongly interacts with the surfactant, in our case Span-80, and later adsorption of surfactant on the membrane walls results in the destabilization of the emulsion. This results in phase separation between the oil and water since the interfacial tension between the two substances rise without an emulsifier prompting immiscibility. Additionally, the hydrophobic surface will attract the toluene molecules, while rejecting water molecules from the surface. The impact of pore size will be important especially when the goal is to increase contact between the surfactant and oil phase with the membrane phase.

For the water-in-decane emulsion, high selectivity for both PVDF-200 PVDF-650 was observed (Figure 4-4). It is noted that all membranes are coated with PVMS prior to use. The narrow porous path allows for greater selectivity, especially given the measured that experimental separation included nanoemulsions (Figure 4-7). However, for the cellulose membrane, it had lower selectivity as shown by the final filtration product in Figure 4-4 The impact of pore size is evident in the water/decane emulsion during the experiment with the water-in-oil quickly permeating through the membrane without any resistance. Prior work by Wang et al.\textsuperscript{131b} using functionalized porous monolith showed that weak interactions between surface and oil prevent effective adsorption of the
surfactant into the pores. With the large fibrous pores for the cellulose membrane, we expect fewer physical interactions between the membrane surface and emulsifier in order to destabilize the water-in-oil emulsion, hence poor selectivity (Figure 4-5).

Figure 4-3 Filtration experiments of water-in-toluene emulsion using the three different membrane type all coated with PVMS
Figure 4-4 Filtration experiments of water-in-decane emulsion using the three-different membrane all coated with PVMS

Figure 4-5 Images of the filtrate collection of water-in-decane surfactant-stabilized emulsion after being purified by the following membranes a) PVDF-200 b) PVDF-650 c) Cellulose
a. Water in Toluene

![Graph showing droplet size distribution for water-in-oil emulsion.]

b. Water-in-decane

![Graph showing droplet size distribution for water-in-decane mixture.]

Figure 4-6 Dynamic light scattering images of the emulsion of a. water-in-oil emulsion and b. water-in-decane mixture
3.4 Anti-fouling characteristics of the membrane

Fouling is a common phenomenon in most membranes that happens when certain organic molecules are attracted to the membrane walls. The strong interaction later results in great amounts of material being adsorbed onto the surface which impedes flow. Foul releasing coatings present themselves as an effective method of mitigating organic materials from adsorbing onto the surface or reduce surface interaction between foulant and membrane. When organic materials are deposited on the surface, they weakly adhere to the surface of antifouling materials making it easier to remove by light brushing, water spray, or hydrodynamic self-cleaning. Silicone materials are observed to possess greater “non-stick” characteristics in comparison to the halogenated chemicals such as fluoropolymer coatings. The improved anti-fouling phenomena is related to the flexibility of the polymeric backbone to allow for interfacial slippage of the material past the surface by reconfiguring the backbone upon shearing. Additionally, incorporating a vinyl pendant group on the PVMS increases the material polarity. During the hydraulic washing, PVMS is deformed using the shear force and this allows the organic material to easily peel or slide off. Experimental results show that after 5 runs, the water-in-toluene and water-in-decane emulsions have the same amount of surfactant composition before and after filtration (Figure 4-3). We hypothesize that while the de-emulsification is happening, the surfactant remains in the toluene and flows through the membrane, while the water is prevented from permeating through. NMR was used to just this concept with the present of surfactant remaining in either toluene or decane solvent (Figure 4-7).
Figure 4-2 NMR image to quantify the surfactant amount prior and after membrane filtration

4. Conclusion

The development of nanoporous was first implemented as in Figure A-1. However, challenges in withholding the thin film of the substate resulted in the film pilling off after use. TEM images of the pilled of were taken to prove nanopores were made as in Figure A-2. Despite the failure in using thin films on microporous support for water-in-oil separation; the project diverted into using microporous membranes instead. A
fundamental understanding of both the limitations between pore diameter and anti-fouling resistance is desired for effective membrane applications in water/oil separations. By using a PVMS coating on a PVDF membrane, we combine both the mechanical strength and rigidity of PVDF substrate with the anti-fouling and hydrophobic nature of PVMS. The interaction between the PVMS and the emulsion dictates whether the purity of the solvent after purification is efficient. Additionally, by reducing the pore size we achieve high selectivity. Finally, PVMS is proven to be anti-fouling surface and NMR result provided evidence that the surfactant can be back-washed after adsorbing on to the surface by using organic solvent already present in the emulsion.
Chapter 5 : Conclusion and Future work

The previous three chapters of this thesis have focused on using primary principles of BCP self-assembly to further expand on the development of siloxane copolymers with large enough Flory-Huggins parameter ($\chi$), while still phase separating with low molecular weight. The expansion in the field is important in the sectors of both the lithographic industry and membrane technology. In using poly(vinylmethylsiloxane), we retain various beneficially properties such as antifouling – which is relevant for membrane application – and improved mechanical properties from cross-linking the matrix after self-assembling.

In the second chapter that delves into thin film studies of PVMS-$b$-PMMA, we approach the project aiming to develop sub-10 nm nanoporous films. The earlier developmental work using poly(dimethylsiloxane-$b$-methylmethacrylate) showed that the polymer has an effective $\chi \sim 0.2$, which is substantial enough to allow phase separation of BCPs with $M_n$ below 10 kg/mol. In this work, we earlier focused on making thicker films of larger than 100 nm as we believed this would be ideal when trying to transfer the material into the nanoporous membrane project.

Solvent annealing was performed first with one solvent, however, the poor order structures led us to believe this was not the optimum method. The low surface energy of the PVMS block results in preferential wetting on at both the substrate and free surfaces. Despite being able to control the free-surface with acetone vapor, this method was unable to neutralize the silicon wafer substrate. We later decided to select a surface neutralizing polymer that would allow both blocks of the copolymer to be present at the substrate by lowering the surface energy difference between each polymer and substrate.
This method did allow us to form perpendicular cylinders, but only at specific cosolvent composition and film thickness. This was confirmed by atomic force microscopy (AFM); however, due to the mobility of the majority PVMS in the film, the material was still able to have several defects during the deswelling, hence poor order across the film. Grazing incidence small-angle X-ray (GISAXS) showed poor ordering with an arc formation indicating a mixture of both parallel and perpendicular morphology. To cater for this issue, we utilized *in situ* cross-linking of the film immediately after the solvent annealing time. The topography of bulk films was additionally looked at by transmission electron microscopy (TEM) and we observed cylindrical holes in the film indicative of perpendicular cylinders through the film. Throughout the process, we were also forced to understand the optimum solvent composition to allow for both polymers present to uniformly orient to both free-surface and substrate while using a neutralizing bottom coat. The impact of both solvent composition and swelling ratio were important factors, especially when trying to obtain desired morphology. It has been observed that during the swelling, the polymer composition changes and this is also of concern, especially if over swelling results in changing of polymer morphology. Upon competition of the study, we were able to show the optimum swelling ratio, film thickness, and solvent composition to retain a uniform morphology.

Future work will involve functionalizing the pendant vinyl group on PVMS to further understand the impact of different groups on the interaction parameter ($\chi$) and morphological effects. For the semiconductor industry to continuously follow through on Moore’s law, shorter polymers that require less processing time for self-assembling and
smaller feature sizes are required. Post-modification of already strong segregating materials can push towards below sub-10 nm nanostructures.

In the third chapter, cyclic block copolymers are a new class of polymers with physical and chemical benefits yet to be fully explored. In thin films, the ability to suppression glass transition temperature ($T_g$) perturbation is of importance, especially when dealing with lithographical templates and polymer coatings. The lack of chain ends is responsible for the reduced conformational configurations a cyclic molecule can attain. Additionally, the improved packing, as has already been observed in cyclic molecules, was of interest to us, especially as we look forward to understanding the impact of blending cyclic block copolymers with linear diblock copolymer on morphology, order-disorder transition, and domain spacing. In order to develop this polymer, we combined several polymerization techniques that allow us to control the final molecular weight and molecular weight distribution. We used anionic polymerization, atom transfer radical polymerization (ATRP), and lastly “click” chemistry to join the homopolymer blocks together to form cyclic-PVMS-b-PMMA. The “click” reaction was done at room temperature under argon. We added a reducing agent into the flask to ensure regeneration of copper(I) is present that allows for the Huisgen 1,3 cycloaddition. The concentration of total homopolymers in the flask was varied based on literature values to determine when the linear impurities are present. In completing the project to obtain the final cyclic material, prep-GPC was needed for final purification based on its ability to separate materials based on the elution time/molecular weight. NMR, IR, GPC, and MALDI were quintessential in confirming end-group functionality and reaction progress. Future
work should look at understanding the impact of topology on phase behavior, domain spacing, nanoconfinement in thin films (10-100 nm), and the impact of chain topology on the order-disorder transition. This work is fundamentally important due to the desire for smaller feature sizes in BCPs. As a result, we used controlled polymerization to control both the final molecular weight and polydispersity.

In the final chapter, microporous membranes were explored for purifying the oil phase of water-in-oil emulsions. Separation of water-in-oil emulsions has primarily focused on the non-surfactant stabilized emulsion. In addition to that, crude oil contains several components such as asphaltenes that are similar in nature as most surfactants and their ability to stabilize emulsion makes them harder to separate mixtures. Surfactants pose a challenge to most separation methods because of surfactants foul membrane surfaces. Fouling is the result of materials adsorbing on to the surface which allows for the emulsion to separate into the water-in-oil mixture which can easily be separated by gravity based separation. Additionally, the mobility of the PVMS backbone allows for easy detachment of the surfactant from the surface with time as the organic solvent washes past it through desorption. This process impacts both selectivity and flux through the membrane. Selection of membrane materials that both allow for anti-fouling capability and retention of the desired interactions with organic solvents is desired.

While performing these experiments, we initially aimed to develop nanoporous membranes using PVMS-\textit{b}-PMMA cast on top of a PVDF support. The support was ideally meant to allow for improved mechanical integrity especially when operating at high flux and pressure. We also opted to cross-link a PVMS thin layer on top of the PVDF membrane.
to ensure good adhesion between the polymer and surface. While developing the polymeric film over the support membrane, we systematically investigated the fabrication steps by SEM to ensure the polymer is always present. Finally, we crosslinked the film onto the support and began testing the system. We witnessed crack formation in the nanoporous cross-linked PVMS - post-etching out the PMMA component - film during the gravity-based filtration, however, the membrane still retained high selectivity. Upon careful observation during the experiment, the PVDF membrane seemed to contract and expand which adversely affects the ability of cross-linked PVMS from attaching on to the support membrane. Thus, we instead shifted the focus of our research on this observation into just using a PVMS coating on the PVDF membrane. In this, we aimed at avoiding detachment of the film from the membrane after several uses. In the study, we used membranes of different pore sizes to test the impact of pore size on effective separation using PVMS-coated support membranes.

Porous membranes of PVDF with pore diameters ranging from 1-3 μm were used both of different surface chemistry with one being hydrophobic and other hydrophilic. The other membrane selected was a microporous cellulose membrane of about 50 μm pore diameter. In the following studies, we employed toluene and decane based on their different spreading parameters with water, and due to the different chemical structures which could affect their interactions with the membrane surface. During the process of separating water-in-oil emulsions, the emulsifier must be adsorbed onto the surface to allow for one component to permeate through, while the other is rejected. This process of demulsification serves to both destabilize the nanoemulsion, hence they are able to
coagulate and finally phase separate into two phases with the organic solvent flowing through the membrane. Additionally, the surfactant can easily be desorbed given the flexible backbone of PVMS allowing for the effective release of surfactant into the organic liquid flowing through the membrane. In performing the experiments, we witness that pore size had an impact on selectivity with the larger PVMS coated cellulose membranes always having poor separation. In the experiment, we selected two solvents with different emulsion stability. As a result of our work focusing on the destabilization of emulsions into water and oil mixtures. We are prompted to further understand if using solvents with a different spreading parameter with regard to water will impact the selectivity upon filtration. Finally, experiments were conducted with undecanethiol functionalized onto the PVMS coated cellulose membrane and we still obtained a poor separation. This led us to believe the pore size allows for effective interaction between the emulsion and membrane substrate, which allows for effective separation of the nanoemulsion. When the pore size is too large then the nanoemulsions will easily flow past the membrane without breaking down into two phases.

Finally, we looked at the NMR images after water-in-oil separation to identify the purity of the material and the impressive antifouling nature of the PVMS coated PVDF-200 and PVDF-650 membranes allowed us to believe it was an effective candidate for mitigating the surfactant from permanently binding to the surface. The ability of the PVMS to deform allows any bound molecules to slip or peel off, and this can later be dissolved by the solvent and flown through the membrane. This work results in a deeper understanding of the impact of pore size and surface functionality are for the separation
of a water-in-oil emulsion. However, different functionality of the membrane surface is still required to find an optimum surface that allows mixtures of solvents to be separated from the water. In several operational scenarios, there is an inherent need for improved flux, hence reducing the pore size does not seem to be a viable method as this will only result in higher transmembrane pressure for operation.

The continuation of the membrane project will involve using a more rigid membrane that does not swell when exposed to the solvent. The swelling of the support membrane resulted in detachment and for us to further study nanoporous thin films, we will need to halt this from happening. Also, during the experiments, creaming was observed. As the oil phase permeates through the membrane, the composition in the flask shifts from majority oil to being majority water. This allows water droplets to begin coalescing and due to the surfactant being nonionic, we believe precipitation and instability in the emulsion droplets begin to occur. To prevent creaming from affecting flux, we would aim at using a cross-flow system in which the flow is in continuous motion, hence this prevents the water from covering the hydrophobic membrane.
Appendix A

Table A-1 Library of the polymers synthesized using anionic, ATRP and “click” chemistry

<table>
<thead>
<tr>
<th>Component</th>
<th>Starting material PVMS molecular weight (kg/mol)</th>
<th>Starting material PMMA molecular weight (kg/mol)</th>
<th>Molecular weight (kg/mol)</th>
<th>Polydispersity</th>
<th>Volume fraction PVMS</th>
<th>Mass of polymer and yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVMS-b-PMMA (242H)</td>
<td>11</td>
<td>10</td>
<td>25.3</td>
<td>1.16</td>
<td>44 %</td>
<td>600 mg (42%)</td>
</tr>
<tr>
<td>PVMS-b-PMMA (242I)</td>
<td>11</td>
<td>6.0</td>
<td>22.0</td>
<td>1.18</td>
<td>46 %</td>
<td>300 mg (25%)</td>
</tr>
<tr>
<td>PVMS-b-PMMA (242L)</td>
<td>11</td>
<td>4</td>
<td>16.4</td>
<td>1.3</td>
<td>69 %</td>
<td>100 mg (8%)</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>10</td>
<td>22.7</td>
<td>1.24</td>
<td>33%</td>
<td>1400 (95%)</td>
</tr>
<tr>
<td>-------------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------------</td>
</tr>
<tr>
<td>PVMS-b-PMMA (241 H)</td>
<td>4.0</td>
<td>3.9</td>
<td>9.1</td>
<td>1.34</td>
<td>52%</td>
<td>700 mg (27%)</td>
</tr>
<tr>
<td>PVMS-b-PMMA (241 L)</td>
<td>11.0</td>
<td>6.0</td>
<td>25.0</td>
<td>1.39</td>
<td>57%</td>
<td>700 mg (24%)</td>
</tr>
<tr>
<td>PVMS-b-PMMA (237 H)</td>
<td>4.3</td>
<td>4.2</td>
<td>12.0</td>
<td>1.48</td>
<td>54%</td>
<td>700 mg (37%)</td>
</tr>
<tr>
<td>PVMS-b-PMMA (237 L)</td>
<td>11.0</td>
<td>6.0</td>
<td>25.0</td>
<td>1.39</td>
<td>57%</td>
<td>700 mg (24%)</td>
</tr>
</tbody>
</table>
Figure A-1 Schematic showing the development of the nanoporous membrane
Prior experiments involved creating a nanoporous membrane that would be placed on top of a nanoporous membrane as in Figure A-1. In the film development stages, the polymeric film was (a) drop-casted on top of a film, (b) solvent annealing, (c) cross-linked with UV at 365 nm at 6 mW/cm² for 10 minutes, (d) exposed to UV at 265 nm for 1 mW/cm² for 20 minutes. Once this was all completed the film was soaked in acetone to dissolve the degraded PMMA.

The weak interaction between the crosslinked PVMS and microporous support membrane resulted in the film pilling off the surface. Despite even coating the PVDF membrane, the film as still pilling off upon exposure to organic solvents. The pilled of the film was collected and placed on a gold TEM grid for imaging as in Figure A-2. The
feature size corresponds to ≈ 20 nm, which is slightly swollen compared to the 13 nm that was observed in dry films in Figure 5-1. As a result of the film pilling off, the project moved on from using a nanoporous membrane film attached to a microporous film into just using a hydrophobic PVMS coating on a PVDF membrane and testing the efficiency of separating nanoemulsions.

Figure A-3 Optical images of the emulsion of a) water-in-toluene emulsion and b) water-in-decane mixture right after mixing and after being left for 24 hrs resulting in demulsification of water-in-toluene, while water-in-decane remains stable.
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