Enhanced Mechanical Performance of Low Dielectric Constant Thin Films Synthesized in Supercritical Co2, and Sans Studies of Microemulsions Induced or Destabilized by Compressed Co2

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ENHANCED MECHANICAL PERFORMANCE OF LOW DIELECTRIC
CONSTANT THIN FILMS SYNTHESIZED IN SUPERCRITICAL CO₂,
AND SANS STUDIES OF MICROEMULSIONS INDUCED OR
DESTABILIZED BY COMPRESSED CO₂

A Dissertation Presented

By

ALVIN HORATIO ROMANG

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
Of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 2012

Department of Chemical Engineering
ENHANCED MECHANICAL PERFORMANCE OF LOW DIELECTRIC CONSTANT THIN FILMS SYNTHESIZED IN SUPERCRITICAL CO₂, AND SANS STUDIES OF MICROEMULSIONS INDUCED OR DESTABILIZED BY COMPRESSED CO₂

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ABSTRACT

ENHANCED MECHANICAL PERFORMANCE OF LOW DIELECTRIC CONSTANT THIN FILMS SYNTHESIZED IN SUPERCritical CO2, AND SANS STUDIES OF MICROEMULSIONS INDUCED OR DESTABILIZED BY COMPRESSED CO2

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Directed by: Professor James J. Watkins

Block copolymer (BCP) phase segregation and self-assembly into two or more distinct domains are primarily dictated by two parameters: the block volume fraction, \( f \), and the product of the segment-segment interaction parameter and the length of polymer chain, \( \chi N \). The volume fraction determines a block copolymer’s phase segregated morphology, whereas \( \chi N \) dictates its overall segregation strength, or phase stability. In order to achieve smaller domain sizes, the interaction parameter must be increased to compensate for the decrease in chain length. In the melt, PEO-b-PPO-b-PEO (Pluronic) triblock copolymer surfactants do not phase segregate primarily due to their low molecular weights and insufficient segregation strength, or low \( \chi N \). Strong hydrogen bonding and
selective interactions of PEO chains with homopolymers capable of hydrogen bonding, such as poly(acrylic acid) were shown to increase the effective segregation strength of the blend. Small angle X-ray scattering demonstrated highly ordered sub-10 nm domains resulting from phase segregation of the blends.

The strong hydrogen bonding interaction between PEO and H-bonding homopolymers was also utilized to incorporate polyhedral oligomeric silsesquioxanes (POSS) into silicate films. In order to improve the compatibility between hydrophobic POSS with hydrophilic Pluronic copolymers, POSS-decorated acrylate monomer was copolymerized with acrylic acid. This eliminated the macrophase segregation between the BCP templates and POSS molecules. The inclusion of POSS is shown to increase the mechanical performance of the low-k films. A supercritical CO$_2$ synthesis route enables the transport of silica precursors into the polymer blends. An increase of hardness of up to 1.8 GPa at $k = 2.4$ and 1.2 GPa for $k = 2.1$ was observed for these mesoporous organosilicate films.

Finally, this work has also focused on the formation of ordered domains of the Pluronic surfactants into a ternary solvent system consisting of two liquid solvents and compressed CO$_2$. Compressed CO$_2$ can influence the compatibility of liquid solvents, inducing phase separation or phase mixing. CO$_2$-induced phase separation of acetone and water and phase mixing of tetradecane and methanol were studied for the formation and breaking of nanoscale domains in the presence of Pluronic surfactants. Long-range ordered structures were observed using small angle neutron scattering.
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CHAPTER 1
INTRODUCTION

1.1 Overview

Engineering nanoscale materials requires significant effort to find intelligent and novel ways to obtain well-ordered materials while keeping the process as simple and cost-effective as possible. Many of the conventional tools and media can be costly and may not be the best solution for future challenges in nanotechnology. One example of the upward trend of the cost curve in nanotechnology can be observed in microelectronic fabrication, which is being addressed by increasing the feature density on the chips.\textsuperscript{1} In order to broadly apply nanoscale materials to manufacturing, such as in photovoltaics and sensors, we must take a different approach in the formation of nanoscale morphologies. Block copolymers (BCPs) provide alternatives to forming nanoscale patterns with tunable size-scale and functionality, while relying on bottom-up synthesis. With the BCP approach however, the method of preserving and transferring BCP structures to useful materials needs to be addressed in order to synthesize useful end products. In this dissertation, we show clever manipulation of the BCPs with homopolymer hydrogen-bonding. This bonding results in a highly-ordered structure using inexpensive polymers and supercritical CO\textsubscript{2} (scCO\textsubscript{2}) synthesis routes, which transfer the BCP structures to inorganic materials. We also demonstrate that the synthesis of mesoporous organosilicate with high mechanical properties relying on the BCP/homopolymer blends and the scCO\textsubscript{2} route.
Supercritical CO\(_2\) provides unique characteristics suitable as an enabling medium for rapid fabrication in the nanomanufacturing field.\(^2\) The properties of scCO\(_2\), which lie between the liquid and gas phase, allow for tunable and hybrid properties that are beneficial in material transport and solvent strength. These properties give CO\(_2\) a unique capability to have the liquid-like solvent strength of a small molecule while also having vapor-like transport properties.

Aside from the more classical scCO\(_2\) extraction, current research on using CO\(_2\) as an enabling medium is focused on nanoscale fabrication mainly for the semiconductor industry, photovoltaics and catalysis. Traditionally, the nanoscale fabrication process relies on liquid and gas-phase processes. The liquid-phase processing has the advantage of having high-solute concentrations, while the vapor phase process allows for a dry process and zero surface tension, which eliminates many of the transport limitations of liquid-phase processing. The hybrid nature of scCO\(_2\), having gas-like transport while maintaining liquid-like solvent strength as well as the zero surface tension,\(^3\) allows the fluid to efficiently transport small precursor materials and penetrate into nanoscale materials without disrupting the underlying structures. Much research about the implementation of scCO\(_2\) into nanofabrication have shown the advantages of using CO\(_2\), including metal depositions,\(^4-12\) metal etching,\(^13-17\) photoresist development,\(^18-20\) and porous ultra-low-k film deposition.\(^21-26\)

As a processing solvent, scCO\(_2\) can be advantageous when combined with BCPs. The zero surface tension and high diffusivity\(^27\) of scCO\(_2\) in polymers allows for the processing of preassembled BCPs. The scCO\(_2\) synthesis route,
combined with the ability to tune BCPs to make highly ordered and useful structures, is crucial in integrating the BCPs into nano-scale manufacturing. There are a number of ways to align the BCPs into ordered, periodic structures that can be utilized at the device level, including graphoepitaxy,28-33 electric field,34-39 and chemical surface modification.40-45 These aligned polymers could be further utilized through the scCO₂ process due to the non-invasive nature and high diffusivity of the solvent.

Selective solubility of CO₂ in different liquid solvents can change the relative solubility between two solvents, thus inducing phase separation or phase mixing of the solvents. By taking advantage of the amphiphilic nature of BCPs, stabilizing the two solvent phases forms micro-structured “oil-in-water” and “water-in-oil” emulsions. We find that the emulsions can be formed or broken by inducing the phase segregation or phase mixing of the two solvents through the introduction of compressed CO₂.

1.2 Supercritical CO₂

A supercritical fluid is a material that is heated and pressurized above its critical temperature (T_c) and critical pressure (P_c). Above its critical temperature and pressure, a supercritical fluid exhibits a change in its behavior from discontinuous density when transitioning from gas to liquid as the pressure is increased to a continuous density change in density at above its critical points. This becomes a significant advantage of supercritical fluid as compared to a liquid or gas process. The continuous density function, as controlled by pressure and temperature, allows for the adjustment of solvent strength, and thus control of the
solubility of materials in the supercritical fluid. For example, the CO₂ density as a function of pressure and temperature plot, calculated from the NIST Chemistry Webbook,⁴⁶ (Figure 1.1) shows an example of the continuous density behavior of a supercritical fluid. The density of CO₂ was shown in the graph to be controllable from gas to near-liquid densities through the pressure and temperature. This density control would prove significant in selective dissolution of many inorganic precursors into the mobile phase, while leaving the BCP morphology undisturbed.

Furthermore, the liquid-like solvation advantage is augmented by the vapor-like transport of the fluid. The surface tension of supercritical fluid vanishes to zero as the liquid-state material reaches its critical point. Figure 1.2 shows the surface tension of water, and hexane and CO₂ as they approach their critical temperature. The zero surface tension of supercritical fluids allows for gas-like transport of solute into small, confined geometry. Combined with the aforementioned high density, the high-solute concentration and zero-surface-tension transport properties of supercritical fluids cannot be achieved by either gas or liquid processing methods.

Furthermore, scCO₂ exhibits a useful interaction with most polymers. While the polymers themselves are not soluble in the supercritical fluid, there is a correlation between the CO₂ equilibrium-limited sorption into the polymer and the density of CO₂.⁴⁷ The CO₂ sorption into the polymer increases the diffusivity of small molecules into the polymer matrix²⁷ by increasing the mobility of the polymer chain and reducing the glass-transition temperature.⁴⁸, ⁴⁹ Through an in situ fluorescence experiment, Gupta et al. showed that there was an order of
magnitude increase in the diffusivity of small molecules in polystyrene between 61 bar and 102 bar of CO$_2$ at various temperatures (Figure 1.3). It was also shown that the diffusivity at 102 bar was 5 order of magnitude higher than at ambient conditions.$^{27}$ This increase in diffusivity allows for efficient and uniform transport of inorganic-material precursors into the polymer matrix, minimizing the concentration gradient between the air-polymer and substrate-polymer interfaces. This uniform transport and the relatively high solute concentration of inorganic precursors in scCO$_2$ enable the use of scCO$_2$ in the manufacturing of nanostructured materials through replicating BCP templates in phase-selective deposition of the inorganic materials in the BCPs.

The interaction of CO$_2$ with different organic solvents can be utilized in the nanomaterial’s fabrication. Compressed CO$_2$ is capable of expanding organic solvents by up to 200% by volume,$^{50,51}$ while changing the interaction between two organic solvents.$^{52}$ Others have also shown that the use of CO$_2$ to solvate other molecules or materials can be assisted with the addition of co-solvents, surfactants, and chelating agents.$^{53-56}$ This allows a reduction of waste and environmental impact in semiconductor fabrication. Francis has shown that two solvents can be phase-separated or phase-mixed by the presence of compressed CO$_2.$\textsuperscript{51} Hundreds of solvent pairs were investigated, with each having different phase diagrams showing that the solubility between solvent pairs can be controlled by the introduction of the compressed CO$_2$.\textsuperscript{51}
1.3 Synthesis of Low-k Dielectrics

The requirements for next generation semiconductor chips are dictated mainly by the semiconductor feature size. As the transistor size of the semiconductor chips decreases, better materials for the low-k dielectric are needed to reduce the RC signal delay and increase energy efficiency. As the distance between the interconnects decreases, the effective capacitance of the insulator materials increases. This increase in the capacitance causes increase in the RC signal delay. To reduce the signal delay, better insulator materials need to be used in the fabrication. The insulator materials, called dielectric materials, need to be low in dielectric constant and robust enough to survive the harsh fabrication process. Historically, the dielectric material used in semiconductor fabrication has been SiO₂, (k = 4.0), deposited via vapor method. The first improvement implemented in the semiconductor fabrication was the use of dense organosilicate materials, which allow for reduction of k to around 2.9. As the future devices shrink further, a lower dielectric constant is going to be required to keep up with the chips’ power needs and efficiency. The International Technology Roadmap for Semiconductors projects that the requirement in 2012, for k insulators is that they will have k values between 2.1-2.5 which can be integrated into the current fabrication process.¹

The main driving force for achieving these low-dielectric constants is the introduction of pores into the oxide-barrier layers. Since the bulk dielectric constant of a material is the average of the materials involved, air-- which has a dielectric constant of 1.0-- is the best candidate to create low-k materials. The
Bruggeman’s effective medium approximation can be used to estimate the dielectric constant of silicate materials as compared to the porosity of the films. Figure 1.4 illustrates the dielectric constant and porosity trade-off for silica (k~4.0) and organosilicate materials (k~2.8), as estimated using the Bruggeman’s EMA. However, challenges remain because of the deterioration of mechanical performance of a material as the density of the material decreases. In fact the hardness of a material decreases to the second or third order with respect to the density.

Many different efforts have been taken to increase the mechanical performance of the porous low-k films, including thermal, UV and e-beam curing. This post-treatment of the synthesized films can lead to the increasing density of the films and the destruction of the silicon-oxide bonds. The tradeoff between the densification of the structure and the further condensation of the bonds means that there is an observed dielectric constant of the materials after the post synthesis treatment.

ScCO₂ is an enabling medium in the synthesis of low-k dielectrics using sacrificial BCP as the template. BCPs, as discussed in the following section, can thermodynamically phase segregate, forming two different phases. Using scCO₂, one could utilize this phase segregation to form a highly-ordered porous structure. The BCP template can be infused by the silica precursor utilizing the scCO₂ medium in order to achieve higher diffusion of the precursors, ensuring film uniformity. The sol-gel reaction of silica precursors in the BCP template can be
selective in the hydrophilic region by selectively segregating the acid catalyst into the hydrophilic phase of the BCP.

Pai, et al. have previously studied the infusion and condensation of the silica precursor into the BCP template with the presence of organic acid.\textsuperscript{25, 26} The scCO\textsubscript{2} route allows uniform, well-ordered mesoporous silica films to be synthesized. This synthesis route allows the formation of films with device-level uniformity, low film stress, and better mechanical performance as compared to other deposition techniques. Figure 1.5 shows the generic schematic of the scCO\textsubscript{2} synthesis route, which involves template deposition, annealing, precursor infusion, and film calcination to remove the template. Further study into this deposition technique has resulted in the study of various organosilicate deposition,\textsuperscript{26} the infusion of perpendicular nanochannels\textsuperscript{23} and direct patterning of dielectric barriers.\textsuperscript{21, 22, 24}

1.4 Block Copolymers

A block copolymer is in essence a polymer composed of two or more polymers tethered together into a single chain. The architecture of the polymers and the number of blocks dictates the way the BCP interacts and phase segregates. The phase segregation in the BCPs is governed by the difference in the chemical properties, specifically the compatibility of the blocks. The simplest and most well-studied BCP is the diblock copolymer, which is a BCP with two distinct polymers tethered at a single point. Under the right conditions, upon phase segregation, diblock copolymers form two, distinct phases, consisting of each type of polymer chain.
The phase separation between the two polymers is governed by the interaction parameter between the two chains and the length of the chain. The greater the interaction parameter of the two blocks, the stronger the phase separation that can be achieved. This segregation strength is quantified as \( \chi \) parameter, defined as:

\[
\chi_{AB} = \left( \frac{Z}{k_B T} \right) \left[ \epsilon_{AB} - \frac{1}{2} (\epsilon_{AA} + \epsilon_{BB}) \right].
\] (1.1)

The interaction parameters describe the free energy penalty of monomers A and B in contact with each other. Positive interaction parameters indicate net repulsive energy between the two monomers, and vice versa.

In general, a diblock copolymer forms four types of mesostructures: spheres, cylinders, bicontinuous, and lamellae, depending on the segregation strength and the composition of the BCPs. Figure 1.6 illustrates a generic, diblock copolymer phase diagram calculated from the self-consistent mean-field theory.\(^{73-76}\) The volume fraction (\( f_A \)) of each block is plotted on the x-axis, while the product of segregation strength and degree of polymerization (\( \chi N \)) is plotted on the y-axis. The micro-phase segregated morphology of BCP is dictated by the volume fraction of the blocks. As the BCP moves from zero volume fraction to approximately 0.5, the BCP transitions from disordered to spherical, cylindrical, bicontinuous, and lamellar morphologies. Richer BCP morphologies can be observed with other types of BCPs such as the A-B-C triblock copolymers.\(^{77,78}\)

As prefaced above, the order to disorder transition of a BCP depends strongly on the segregation strength and the molecular weight of the BCP. The domain size of the BCP depends on its chain length, which is proportional to the
BCP’s molecular weight. There is a trade-off between the domain size and the segregation strength. In order to keep decreasing the domain size, a larger interaction parameter is necessary to achieve spontaneous phase segregation of the BCP. Tirumala, et al. showed that polymer blends of relatively weakly-segregated BCP can be enhanced by selective blending of the BCP with a homopolymer.\textsuperscript{79-81} The homopolymer induces the phase segregation by selectively associating with one block of the copolymer while increasing the incompatibility with the second block of the copolymer. This allows the BCP to form a highly-ordered morphology with a domain size as small as 5 nm.

The extension of BCP into the nanotechnology and semiconductor industry has been enabled by different methods of aligning the BCP to the device level structures. The interaction between BCPs and the underlying substrates becomes significant due to the inherently random orientation of the phase-segregated structure in the absence of external force. From the basic copolymer structure of cylindrical, lamellar, and spherical morphology, the alignment of the BCPs can be controlled by changing the interfacial energy between substrate and polymer, manipulating the topography of the substrate, and applying external force to the BCPs. One can manipulate the interfacial energy between the BCPs and the substrate in several ways, including changing the properties of the substrate and manipulating each block’s interaction with the substrate.

The BCP morphology on a substrate depends strongly on the energetics between the polymer-substrate and polymer-air interfaces.\textsuperscript{82-85} At the substrate-polymer interface, the orientation of a BCP depends mainly on the difference in
how the blocks and the substrate interact. For example, a lamellar BCP, such as PS-b-PMMA, prefers to arrange its morphology parallel to the silicon substrate. This arrangement is mainly due to the stronger interaction between the substrate and the PMMA block. However, by changing the surface property of the substrate to be energetically neutral to each block of the copolymer, the orientation of the BCP can be manipulated to be perpendicular to the substrate. The neutral surface can be achieved by grafting a random copolymer brush of the same repeat unit with the BCP and controlling the ratio of the monomers. This creates a zero interfacial energy difference between one block/substrate and the other block/substrate. The neutral interface allows the BCP to align perpendicular to the substrate. However, this perpendicular orientation does not control the orientation of the domain in the lateral direction with respect to the substrate.

The alignment of the BCP can be induced by selectively modifying the substrate chemically. The previous neutral brush techniques allow alignment in z-direction, while lacking in the x and y directions. Changing the chemical properties of the substrate selectively allows the control of the BCP in the lateral directions. The chemical patterning of the substrate to align the BCP relies on the premise of changing a region of the substrate to preferentially interact with one of the blocks of the BCP. This method combines the self-assembly of block copolymer and top-down photolithography patterning methods. Nealey and coworkers showed that the lithography technique creates patterned substrate that can align the phase-separated BCP to device-level patterning.
outlines the direct patterning method using polystyrene as the monolayer and PS-PMAA as the aligned BCP. Direct patterning relies on the alteration of the hydrophobicity of the polystyrene monolayer through region-selective oxygen plasma. The oxygen plasma changes the hydrophobic nature of the polystyrene monolayer to be more hydrophilic. This creates a thermodynamic force that, upon annealing, aligns the PS block onto the untreated region and PMAA to the oxygen plasma-treated region.

1.5 Dissertation Goal

The focus and goal of this dissertation is to study and utilize the BCP and blends of BCPs and homopolymers to synthesize nanostructured materials—mainly the low-k dielectric layer. We study the selective hydrogen-bonding interactions between the homopolymers and BCPs in the blends to understand the change in the segregation strength of the BCPs and the resulting phase-separated structures. This study will show the selective segregation through increases the apparent $\chi$ of the BCP which drives the phase segregation of the otherwise phase-mixed BCP. This increase in $\chi$ also enables the formation of domain size of less than 5 nm and improves the long-range order of the studied BCPs.

The other advantage of studying this interaction of homopolymer-BCPs is the ability to utilize the hydrogen-bonding interaction to enable mixing between less favorable polymers. In an effort to enhance the mechanical performance of the low-k insulation layer, we explore the blending of polyoligomeric silsesquioxane silicate particles into the block copolymer through this hydrogen bonding. We identified the scCO$_2$ synthesis route as the enabling step for our
research, due to the steps for silica condensation and the separation of the template formation. This separation allows for the uniform dispersion of silica particles into templates before the silica condensation.

Finally, this study will also focus on the BCP surfactant interactions with the ternary system of two-solvents and compressed CO$_2$ in forming stable surfactant systems. It will also focus on breaking stable surfactant systems using compressed CO$_2$. The ability of CO$_2$ to change the interaction between solvents allows us to manipulate the structure and to tune the strength of the interaction between the two fluid-phases stabilized by the surfactant.
Figure 1.1. A plot of the densities of CO₂ as a function of the pressure at three different temperatures. A continuous CO₂ density ranging from gas to liquid-like can be achieved by varying the pressure and temperature.⁴⁴
Figure 1.2. A plot of the surface tension of water, hexane and CO$_2$, showing the disappearance of the surface tension as the materials reach their critical points.\textsuperscript{44}
Figure 1.3 Decacyclene diffusion in CO$_2$-swollen polystyrene as a function of weight fraction of CO$_2$ at 55 (●), 65 (■), and 70 °C (▲).$^{27}$
Figure 1.4. Plot of dielectric constant as a function of porosity for silica ($k \approx 4.0$) and organosilicate ($k \approx 2.8$), estimated by Bruggeman's effective medium approximation. Adapted from Ref 52.
Figure 1.5. Schematic drawing of scCO$_2$ synthesis route of mesoporous silica films.$^{24}$
Figure 1.6. Phase diagram of a diblock copolymer plotted as a function of the segregation strength and volume fraction. The phase diagram is calculated from the self-consistent mean-field theory.\textsuperscript{73}
Figure 1.7. Schematic and top down SEM image of directed assembly of block copolymers on silicon substrates.\textsuperscript{43}
1.6 References


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CHAPTER 2
WELL-ORDERED TRIBLOCK COPOLYMERS FROM BLENDING
WITH HYDROGEN BONDING HOMOPOLYMERS IN MELT

2.1 Introduction

The phase segregation of block copolymers (BCPs) into micro domains has long attracted research interests.\(^1-^5\) BCPs have been used as the structure-directing agent for the synthesis of nanostructured materials both in solution\(^6-^{11}\) as well as in melt.\(^12-^{17}\) One of the main hurdles in high-throughput industrial production of nanostructured materials using block copolymers is that the synthesis of BCPs can be costly. For larger industrial production, one can turn to readily-available non-ionic surfactants such as the PEO-b-PPO-b-PEO copolymer, available under the Pluronic® trade name. The Pluronic BCP surfactants are available in various molecular weights and compositions. However, in melt, the segregation strength between the PEO and PPO blocks of Pluronic is not high enough for spontaneous phase segregation, especially with BCPs of lower molecular weight at ambient conditions.\(^18\)

The spontaneous segregation of block copolymers into well-defined periodic morphologies is governed mainly by three parameters: the segment-segment interaction parameter (\(\chi\)), the number of monomers on the polymer chain (\(N\)), and the composition of the copolymer (\(f\)).\(^1\) These parameters govern the phase segregation and the morphology of the BCPs. The product of interaction parameter (\(\chi\)) and degree of polymerization (\(N\)) are the controlling parameters of
the transition of the block copolymer from phase mix and phase segregated in melt. A phase-separated BCP requires this $\chi N$ to be above a certain critical number. The interaction parameters are governed by the chemical composition of the chain segments, such that the only way to induce phase segregation without changing the chemical composition of the chains is by increasing the molecular weight of the polymers. However, as the requirement for domain size decreases, overall molecular weight of the BCPs also needs to decrease.

PEO-b-PPO-b-PEO is relatively inexpensive and available in bulk quantity, making it a prime candidate for templating materials in high-volume nanomanufacturing. The PEO domain of the Pluronic surfactant has a relatively low melting point (~60 °C). It can be easily processed at slightly elevated temperatures and readily phase separate without much annealing time due to the low glass transition temperature. The challenge in using this polymer is to create a phase-segregated block copolymer, while suppressing the crystallization of the polymer. Depending on the application, suppressing crystallization could be crucial in achieving the well-ordered structure because the crystallization could disturb the microphase segregation of the well-ordered polymers.\textsuperscript{19}

Although the Pluronic surfactant is capable of forming a sub-10 nm structure, the $\chi N$ of this polymer is not sufficiently high to phase segregate in its melt form due to the low molecular weight and the relatively small dissimilarity between the PEO and PPO ($\chi_{\text{PEO-PPO}} \sim 0.066-0.068$ at 80 °C).\textsuperscript{18, 20} The interaction parameter can be calculated through:\textsuperscript{18}

$$\chi(T) = (-0.122 \pm 0.022) + \frac{66.8 \pm 8.2}{T}$$ \hspace{1cm} (2.1)
The $\chi N$'s for the two systems in this study were calculated to be 10.5 for the Pluronic P105 and 5.75 for L92 at room temperature, while the critical $\chi N$'s of the system required to reach spontaneous phase segregation are 19 and 40, respectively. This meant both block copolymers were above their order-to-disorder transition temperatures at room temperature.

The blending of block copolymer and homopolymer has been shown to alter the apparent interaction parameter between the blocks$^{21, 22}$ and suppress the crystallization of the PEO block.$^{23}$ Furthermore, the phase segregation of BCPs has been shown to be induced by the hydrogen bonding of one block to small molecules.$^{24, 25}$ The strong interaction through hydrogen bonding can be selective in nature, which favors one block of the BCPs and alters the apparent interaction parameters between the two phases of the BCPs. The change in the interaction parameter is especially significant when the homopolymer strongly associates with one of the blocks. In this case, we found that the segregation of these low molecular block copolymers can be enhanced significantly by blending a homopolymer that strongly interacts with one of the blocks-- the PEO block of the Pluronic BCPs. The selective interaction of the PEO to the homopolymer effectively increases the overall segregation strength between the blocks in the polymer, resulting in a spontaneous, thermodynamically-stable, phase-segregated system at low molecular weight. The low molecular weight allows for the block copolymer to form a highly-ordered morphology at very small domain sizes.
2.2 Experimental

2.2.1 Chemicals

PEO-b-PPO-b-PEO block copolymers were graciously provided by BASF. The Pluronic surfactants are available in a variety of molecular weights and compositions. Pluronic P105 (PEO₃₆-b-PPO₅₆-b-PEO₃₆) has a number average molecular weight of 6500 g/mol and PDI of 1.26. This polymer is solid at room temperature due to the presence of a PEO chain at 50 wt%, which crystallizes. Pluronic L92 (PEO₈-b-PPO₅₀-b-PEO₈) has a majority of PPO at 80 wt%, with number average molecular weight of 3650 g/mol, with PDI of 1.12. Pluronic L92 is liquid at room temperature. Poly (acrylic acid) was obtained from sigma Aldrich; it had a number average molecular weight of 1000 g/mol, and PDI of 1.8. We obtained PAA homopolymers of a higher molecular weight from Polymer Source (88 kg/mol PDI: 1.12, 44 kg/mol PDI: 1.08, 20 kg/mol PDI: 1.25 and 8500 g/mol PDI:1.07). Finally, Cobalt(II) acetate was purchased from Fisher Scientific.

2.2.2 Small Angle X-ray Scattering

Small-angle x-ray scattering (SAXS) was used to study and analyze the structure and characteristics of materials in nanoscale range. X-ray scattering patterns obtained by the method can be translated into the structural information of the materials. Depending on the domain size, the x-ray scattering experiments can be tailored appropriately, from wide angle to ultra-small angle scattering. Small-angle x-ray scattering is typically used for characterizing materials in the order of 3-50 nanometers, while smaller and larger size scales are possible depending on the positioning of the detector.
SAXS relies on the difference in the electron density of the materials to establish the scattering contrast. The interaction of the x-ray with the material is between the material electron and the electromagnetic wave of the x-ray. Hence, the electron density of the materials gives rise to the scattering of the x-ray by the sample. While most of incident beam is transmitted through the samples, some of the x-ray is scattered. The distribution of electron density through the samples gives rise to the observed spectra. This means the x-ray can only detect a material with differences in the electron density of the materials, not the material structure itself. It is conceivable that an ordered structure does not give x-ray scattering spectra due to the lack of the contrast in electron density. The average electron density can be calculated from the following:

$$\rho = Z_m \rho_m = N_A \frac{Z_M}{M_M} \rho_m$$

where the electron density ($\rho$) is a product of the mass density ($\rho_m$) multiplied by the electron per mass ($Z_m$). $Z_m$ can further be broken down into a function of the Avogadro’s number ($N_A$), the number of electrons per molecule or monomer unit, ($Z_M$), and the molecular weight of the molecule or monomer unit ($M_M$).

For BCPs and their blends, the scattering pattern resulting from the SAXS is similar to solid crystallography. The x-ray scattering analysis follows Bragg’s law. The constructive and destructive interference of the electromagnetic wave from the x-ray source creates the patterns observable in the resulting spectra. The spectra follow Bragg’s law is

$$n\lambda = 2d \sin \theta$$
where $n$ is the integer, $\lambda$ is the source wave length, $d$ is the center-to-center distance of two adjacent domains, and $\theta$ is half of the angle of scattered beam to the source. The diffraction pattern from the x-ray can provide us with the structural information of the materials, such as the center-to-center distance of the domains (d-spacing) and the packing morphology of the materials. As mentioned in Chapter 1, BCPs above their critical segregation strength phase segregate into four different morphologies: lamellae, cylinder, spheres and bicontinuous. The scattering spectra of ordered materials are composed of the Bragg diffraction peaks. The first and strongest peak is the primary scattering peak corresponding to the $n=1$ integer of the Bragg’s law equation. The higher order reflection peaks and their subsequent ratios can be used to determine the morphology of the materials. A bcc spherical morphology gives the peak location ratio of $1:\sqrt{2}:\sqrt{3}:\sqrt{4}...$, hexagonally packed cylindrical $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}...$, and lamellar $1:2:3:4...$. The higher-order reflection peaks arise from the interference of waves from further domains. Thus, the appearance of higher-order reflection peaks convey how well-ordered the materials are.

The small angle x-ray scattering in this work was done on a Rigaku-Molecular Metrology SAXS equipment in the W.M. Keck Nanostructures Laboratory at the University of Massachusetts. Samples were prepared from concentrated solutions of the polymer and polymer mixtures in ethanol and small amounts of water. The samples were then drop-casted onto a 1-mm thick washer, sandwiched between two Kapton® films. The samples were dried at 80 °C under vacuum overnight. The top Kapton® film was then glued onto the washer to keep
polymer melts from flowing out of the holder. The data collection was done at 80 °C to make sure that the samples were at melt state. All data collections were done at constant time (45 minutes). The constant path length provided by the washer mount and the relatively constant data collection time led to quantitative comparisons between spectra.

2.3 Results and Discussion

The phase separation behavior and the structures of Pluronic BCPs blended with PAA were examined in melt through SAXS. Above their melting temperatures, the crystallization of PEO did not affect the resulting spectra. In this work, Pluronic P105, L92 and their blends with PAA were studied, to represent PEO in the continuous domain and in the minority domain respectively. The selective association between the PEO and PAA chains26-28 suggests that the difference between chain conformation of PEO and PAA in the continuous phase and minority phase affects the phase behavior of the blends. Furthermore, the phase behavior of Pluronic in the presence of different PAA chain length would show the enthalpic and entropic contribution of the chain conformation in the PEO domain.

Figure 2.1a. shows that the SAXS spectra of Pluronic P105 and PAA (1800 g/mol) blends with concentrations from neat P105 control to 50 wt% PAA. The blends of Pluronic and PAA in melt show the appearance of the primary scattering intensity indicating the microphase segregation between the PEO and PPO chains with the presence of PAA. The control of Pluronic P105 did not show any appreciable primary scattering peak, indicating that the BCP was in a
disordered state. At 10 wt% mixture, a broad primary peak appeared, indicating that the polymer blend started to phase segregate in melt; however, because the segregation strength between the two chains was weak, no higher-order reflection was observed. The contrast of the scattering arose from the difference of electron density between the two domains, suggesting that the PAA selectively segregates into the PEO domain. As the concentration of PAA was increased from 10 wt% to 20 wt%, the primary peak became significantly sharper, indicating a strong segregation of the PEO+PAA domain from the PPO domain. A weak second-order reflection was also observed at the 20 wt%, indicating that P105-PAA blends, forming a longer-range order.

At 30 wt% loading, however, the second order reflection peak became unnoticeable, while there was a slight change in the primary peak position. As the PAA concentration was increased to 40 wt% and 50 wt%, the second-order reflection reappeared at $\sqrt{4q^*}$. Additionally, a third-order reflection also appeared at $\sqrt{7q^*}$, which indicated that the P105-PAA blends at these concentrations were in cylindrical morphology. The $\sqrt{7q^*}$ was not observed at lower concentrations--significantly at 20 wt% concentration--which showed one second-order reflection at $\sqrt{4q^*}$. This appearance of a third peak suggests that the BCP-PAA blends underwent an order-to-order transition from lamellae to cylindrical morphologies. It is also interesting to note that the domain spacing of the P105-PAA blends do not significantly change as the PAA concentration was significantly increased. Figure 2.1b. is a plot of full width of half maximum (FWHM) of the primary peaks of the SAXS spectra as a function of PAA concentrations. The decrease in
FWHM between a PAA concentration of 10% and 20% indicates the increase in the order of the microphase-separated domains.

To study the strength of hydrogen bonding between PAA and Pluronic BCPs, one can study the effect of confinement of a PAA chain in the PEO domain. In the previous study, relatively low, short-chained PAA, with a number average molecular weight of 1000 g/mol, was used in the blends. By using longer-chained PAA, one can study the effect of confinement and the trade-off between the enthalpy of hydrogen bonding and the entropy of chain stretching. Figure 2.2 shows the x-ray scattering pattern of Pluronic P105 blended with PAA at 30 wt% having number average molecular weights ranging from 1,000 g/mol up to 88,000 g/mol. These PAAs have a narrow molecular-weight distribution, except for the 1,000 g/mol by comparison. These blends exhibited similar behavior to the 1,000 g/mol PAA. The blends exhibited a high degree of phase segregation and long-range order as reflected by the higher-order reflection on the Bragg diffraction pattern. The similar behavior between PAA at the low molecular weight of 1,000 g/mol to a much higher one of 88,000 g/mol suggest that the blends are insensitive to the molecular weight, and that the enthalpic contribution from the hydrogen bonding is larger than the penalty of the chain stretching of the homopolymers, even at 88,000 g/mol PAA. Table 2.1 shows the molecular weight and radius of gyration of the PAA homopolymers that were used in this experiment. The radius gyrations of these PAAs indicate that the PAA coils are larger than the domain size of the P105 (~5 nm), suggesting that the chains are stretched under the confinement. This means the enthalpic contribution to the
hydrogen bonding was higher than the entropic penalty of the chain stretching to the PAA chain at a molecular weight up to 88 kg/mol. The USAXS study showed that macrophase separation of the BCP blend was not observed. Furthermore, by calculating the d-spacing from the primary peak position, the domain spacings of the blends vary only slightly—between 10.2 and 11 nm for the wide range of PAA molecular weight. The insensitivity of the phase segregation to the molecular weight of PAA suggests that the molecular weight variation in hydrogen-bonding homopolymer does not play a crucial role in the interaction and phase segregation, allowing a non-specialized polymer to be used in the blends’ applications.

The reverse composition of PEO in minority, discontinuous phase forces the PAA in confinement within the expected spherical morphology of the BCP. Pluronic L92 is a PPO majority BCP, with a very short chain of PEO (PEO molecular weight of ~730 g/mol). At around 20 wt% of PEO, the morphology of the BCP is expected to be spherical with PEO in the minority domain. The short PEO chain means that L92 is in liquid state at room temperature due to the depression of melting temperature as a function of molecular weight. The liquid state of the L92 and its blends would show in the broader SAXS spectra because of the mobility of the domains and the lack of long range order correlation. The low molecular weight of the L92 also means that the overall segregation strength between the two polymer blocks is lower than the P105.

Figure 2.3a shows the SAXS spectra of L92-PAA blends (1,000 g/mol). The neat L92 did not show any correlation peak, suggesting that there was no
phase segregation in the BCP. The addition of PAA by 10 wt% did not significantly alter the SAXS spectra. The addition of PAA at 20 wt% caused the appearance of a weak peak, while the addition of 30 wt% and 40 wt% further increased the peak height and sharpness. At 20 wt% PAA, the addition of PAA started to show the compositional fluctuation of the scattering contrast in the disordered state of the BCP blends. The further increase in peak height indicates an increase in concentration and order of the contrast due to the phase segregation of the BCP. Further increases in PAA concentration to 50 wt% decrease the peak height of the spectra. The plot of FWHM of the L92-PAA blends shows that the FWHM decreases as the concentration of PAA increases up to around 30 wt% of PAA. At 40 and 50 wt% PAA, the FWHM shows increases indicating decrease in correlation between the domains (Figure 2.3b). This decrease suggests that there was a disruption of the ordered structure of the BCP blends. As previously indicated, the decrease in the segregation was not observed in the PEO majority Pluronic (such as the F108 and the P105). The decrease in the segregation strength as the PAA concentration was increased can be attributed to the increases of confinement of PAA in the PEO region, as well as the exhaustion of available ether oxygen group in the PEO to hydrogen bond with PAA. The hydrogen bonding between ether oxygen atoms and the acrylic acid was also shown to be energetically favorable to different ether oxygen groups in polymers. The selective segregation of PAA into the PEO region is attributed to the more thermodynamically stable configuration of PAA that interacts with the PEO rather than PPO. The confinement of the PAA into the PEO discontinuous minority
domain in L92 could disrupt the selectivity of the PAA into PEO. An order-to-order transition could also result in the change of the SAXS spectra observed.

In our study, the improvement in the phase separation of the L92, however, did not extend to the long-range order of the mesostructure. The SAXS spectra did not show any second-order reflection peak, which is the indicator of a long-range ordered system. This is in contrast with the F108 and P105, which showed the long-range, ordered behavior. There are several possible explanations for the lack of second-order reflection in the scattering spectra: the mobility of the polymer due to the liquid nature of the BCP blend (which is similarly observed in the microemulsion systems), the short chain of the PEO/homopolymer blends in the BCP, allowing more flexibility of the morphology due to the PPO chain, or the lower segregation strength of the polymer due to the short nature of the BCP.

The addition of a selective hydrogen-bonding homopolymer (in this study PAA), to the BCP will improve the effective segregation strength of the BCP. The selective association of PAA into the PEO block of the BCP can be deduced by observing the order-to-order transition of the P105-PAA blends from lamellar morphology to the cylindrical morphology. This order-to-order transition can be explained by the increase in the overall volume fraction of the PEO side due to the selective segregation of the PAA into the PEO domain. The primary peak positions of both P105/PAA and L92/PAA blends stay constant even as the volume fraction of one block of BCP in both the minority and majority domains increases. One implication of the lack of change in the domain spacing of the
polymer blends is that there is an increase in the sharpness of the domain boundary.

2.4 Application of the Blends

One attraction for using the Pluronic/homopolymer blends for producing highly-ordered nano-scale structures is that the BCP could produce very small domain space and a highly-ordered meso-structure. Among other things, these properties make the Pluronic/homopolymer blends suitable as templates for inorganic mesoporous materials and as high volume nano-scaled materials. One application that can benefit from the domain size is the synthesis of mesoporous amorphous silica films, which have applications in microelectronics, fluidics, catalysis, etc. One can envision a phase-selective synthesis process utilizing the hydrophobic-hydrophilic difference between the PEO and PPO domains in melt. Our group has previously studied phase-selective metal oxide deposition into BCP melt. Further discussion of the phase-selective silica deposition is described on Chapter 3.

The long-range order of the BCP can be observed in the mesoporous silica films, which were synthesized using the BCP blends as the sacrificial template. Figure 2.4 shows the transmission SAXS of the mesoporous silica synthesized using Pluronic F127/Polyhydroxy-styrene (PHS) as the template. The synthesis detail is will be discuss the next chapter. PHS has the capability to hydrogen bond with PEO chain with similar results as the PAA. Combined with F127, the blends can produce a highly-ordered cylindrical mesostructure that is parallel to the substrate. The transmission 2-D detector images of the transmission SAXS of
the silica films were taken at two incidence angles relative to the substrate. Figure 2.4A is the spectra of the silica film taken at 10°, while Figure 2.4B shows the spectra taken at 90° incidence angles. The difference in the spectra can be explained by the orientation of the cylinders with respect to the substrate. At 10° incidence angle, the spectra shows hexagonally-distributed, scattering peaks, which indicate that there are a long-ranged, ordered 3-D structure, with the majority of the pores oriented parallel to the substrate. A single diffraction ring was observed at the 90° incidence angle, suggesting that the orientation in the plane of the films is random.

There have also been many studies of metal/block copolymer nanocomposites. The localization of the metal in the block copolymer relies on the solubility of the metal, the metal ligand complex, or the affinity of the metal and its complex with the unpaired electron. The blending of Pluronic L92 BCP with PAA provides a localization of negatively-charged PAA that can selectively attract metal ions into the minority domain. Figure 2.5 is a TEM image of cobalt (II) acetate salt confined in the L92 blend. The composite was casted from a 1% solution of solids in 20/80 wt% water/ethanol. The solids were composed of 10 wt% cobalt acetate in L92/PAA (7:3 wt ratio). The solution was acidified with hydrochloric acid until the metal salt was soluble. Finally, the solution was casted onto the carbon-coated TEM grid.

The localization of the cobalt salt into the minority domain of the L92 block copolymer can be observed in the TEM image. The clusters in the order of 5 nm in the diameter shows the cobalt ion was present only in the minority
domain of the L92/PAA blends. The localization into the minority domain of the
L92/PAA was due to the attraction between the acrylic acid anion and the cobalt
cation.

2.5 Conclusion

The blending of PEO-b-PPO-b-PEO triblock copolymers with hydrogen
bonding homopolymer allows phase segregation of short-chained BCPs in melt.
The PAA interacts strongly with the PEO chain of the BCP, thus increasing the
effective interaction parameter between the PEO and PPO blocks. Two Pluronic
BCPs were studied: P105 and L92. The blending of P105 with PAA shows that
PAA increases the segregation strength as represented by the decrease of FWHMs
of the SAXS spectra, and the appearance of the second and third-order reflection
peaks. The SAXS results suggest that the addition of PAA into P105 BCP results
in well-ordered phase separation between the PEO and PPO domains. We also
observed a similar decrease in FWHM on the SAXS spectra of L92 and PAA
blends; however, we did not observe second-order reflection indicating longer-
range ordered morphology.

The strong phase segregation and the miscibility between the BCP and
homopolymer were utilized as a mesoporous template for small porosity and as a
structure-directing template for polymer metal nanocomposites
Table 2.1 A list of poly(acrylic acid) with number average molecular weights between 1 kg/mol to 88 kg/mol and the corresponding ideal unperturbed radius of gyrations.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$M_n$ (g/mol)</th>
<th>PDI</th>
<th>Ideal unperturbed Rg (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA 1.8k</td>
<td>1,000</td>
<td>1.8</td>
<td>1.52</td>
</tr>
<tr>
<td>PAA 8.5k</td>
<td>8,500</td>
<td>1.07</td>
<td>4.44</td>
</tr>
<tr>
<td>PAA 20k</td>
<td>20,000</td>
<td>1.09</td>
<td>6.8</td>
</tr>
<tr>
<td>PAA 44k</td>
<td>44,000</td>
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</tr>
<tr>
<td>PAA 88k</td>
<td>88,000</td>
<td>1.12</td>
<td>14.3</td>
</tr>
</tbody>
</table>
Figure 2.1 a. SAXS spectra of Pluronic P105 PAA blends from neat P105 to 50 wt% PAA concentrations. b. full width of maximum of the SAXS spectra from a.
Figure 2.2. SAXS spectra of P105 PAA blends at 30 wt% at different molecular weight.
Figure 2.3. a. SAXS spectra of Pluronic L92 PAA Blends with concentrations ranging from neat to 50 wt%. b. Full width of half maximum plotted against the blend concentration, calculated from a.
Figure 2.4. 2-D detector image of transmission SAXS on mesoporous silica films templated from F127/PHS blends at 16.7 wt% PHS concentration. Part A was taken at a 10° incidence angle, part B at 90°.
Figure 2.5. TEM of 10wt% cobalt (II) acetate confined in L92-PAA blends (7:3 wt ratio).
2.6 References


CHAPTER 3

SUPERCRITICAL CO₂ SYNTHESIS OF ENHANCED MECHANICAL PERFORMANCE SILICATE FILMS THROUGH INCORPORATION OF POSS

3.1 Introduction

Historically, microelectronic fabrication has relied heavily on the use of dense SiO₂ as the dielectric insulator between interconnects, mainly for the mechanical properties and robustness of the materials in the process integration. However, as the size scale of the fabrication decreases, the reduction in capacitance of the dielectric insulator becomes significant in reducing signal delay and cross talk. When the industry scaled down to 90-nm nodes, dense organosilicate films (k ~ 2.9) were utilized to increase the chips’ performance.¹,² The organosilicate materials achieve lower dielectric from reduction of the polarizability of the SiO₂ by substituting the Si-O linkage with organic groups. This substitution of the Si-O bonds also introduces the free volume to the silicate films. The small introduction of porosity and the disruption of the Si-O skeletal structure lead to decrease of film modulus from 76 GPa to 16 GPa of silica to organosilicate films respectively.²,³ Further reduction in k is achieved by using porous organosilicate films, and taking advantage of the dielectric of free volume (k = 1).

Since Mobil lab researchers’ invention of MCM-41 porous silica,⁴ many efforts have been focused on the transfer of the highly-ordered porous silica to
the semiconductor industry. The potential of integrating porous silica as the interconnect insulator allows the use of an inorganic SiO\textsubscript{2} skeleton that is thermally stable and mechanically robust, while reducing the dielectric constant through the introduction pores in the matrix. Many efforts have been focused on incorporating the self-assembly nature of ionic and nonionic surfactants to produce well-ordered silicate structures--mainly through spin-coating or dip-coating evaporative-induced self-assembly.\textsuperscript{5-9} However, the main challenge of integrating porous silica into the semiconductor fabrication is how to prevent the significant reduction of mechanical performance in porous materials. Others have shown that mechanical performances of materials decay exponentially as a function of density.\textsuperscript{10, 11}

A second challenge of integrating mesoporous silica films into semiconductor fabrication is repairing the dielectric layer after the etching steps. The etching process damages silicon-oxygen linkages and the organic side group, thus increasing the polarity of the silica film.\textsuperscript{12} Plenty of efforts, either through vapor phase or supercritical CO\textsubscript{2} processes, have been spent to repair the dielectric damage caused by the etching processes.\textsuperscript{13-18} Our group has previously shown, through the direct patterning method, that we can replicate sub-100 nm lines without the etching step.\textsuperscript{19, 20} Directly depositing porous silica into the device-level pattern simplifies the steps. As such, the dielectric constant values of the film remain as the synthesized films--not damaged by etching.

Our group has previously shown the synthesis of well-ordered mesoporous silica based on the sol-gel reaction, utilizing amphiphilic-block copolymers in
supercritical CO$_2$. The pore size, morphology, and backbone chemistry of the mesoporous silica could be tailored by template size, morphology, and the choice of organosilicate precursors. This degree of control could be achieved due to the separation of the template materials and the precursor condensation steps—in contrast to other sol gel methods. This separation—where the template of the porous materials is formed separately from the condensation of the silicate precursors—also provided one significant advantage: This separation template and formation of the silicate structure allowed the pre-formation of the template for device-level template replication, and also allowed us to tailor the template to enhance the properties of the silica materials.

In this work, we focused on integrating the POSS cage into the silica backbone to improve the mechanical properties of the silica synthesized in the supercritical CO$_2$ method. The incorporation of POSS into the template materials allowed us to tailor the mechanical properties of the materials by dispersing the POSS uniformly throughout the silica films. POSS materials have been widely used as additives to mostly-polymer materials to increase the material’s mechanical performance, as well as to stabilize the temperature of the dielectric polymeric barrier.

Through collaboration with the University of Wisconsin-Madison, we conducted a second study into the formation of silica as a dielectric barrier and the direct deposition of silica into directed assembled block copolymer. Block copolymer use in a device is limited by the lack of device-level assembly. Specifically, block copolymers are limited by the lack of orientation control of
pattern on surface. Many efforts to align and orient block copolymers on substrate in order to achieve useful morphology for useful applications.\(^{32-42}\) The directed assembly of block copolymer allows for the alignment of block copolymer to the underlying pattern.\(^{43-46}\) Although the resulting BCP pattern results in similar-characteristic length as the underlying pattern, the use of BCP can reduce the line edge roughness of the resulting pattern. Here, a bottom up approach to the patterning of dielectric layers using the scCO\(_2\) deposition technique is used by taking advantage of the non-trivial nature of the directed assembly pattern and the BCP interface as the boundary for the reduction in line edge roughness.

Using hydrophilic-hydrophobic diblock-copolymers, the direct patterning technique can be utilized in the selective deposition of silica. The ability of the scCO\(_2\)-deposition technique to deposit silica into a pre-arranged template allows for the deposition of silica without disruption to the aligned BCP template. As mentioned above, separating the condensation step and the formation of the template offered an advantage to the scCO\(_2\) deposition method. The supercritical phase deposition allows for rapid diffusion\(^{47}\) of silica and organosilicate precursors\(^{48}\) without disruption of the pre-formed BCP templates.

### 3.2 Experimental

#### 3.2.1 Chemicals

Acryloisobutyl POSS was purchased from Hybrid Plastics. Tetraethyl orthosilicate (99.999%), tert-butyl acrylate, copper(I) bromide, copper(II) bromide, ethyl-2-bromoisobutyrate and N,N,N’,N’’,N’’’-pentamethyldiethylenetriamine were purchased from Sigma Aldrich.
Methyltriethoxysilane was purchased from Gelest, Inc. Ethanol (anhydrous), toluene (ACS grade), dichloromethane (ACS grade) were purchased from Fisher Scientific. p-Toluenesulfonic acid monohydrate and trifluoroacetic acid were purchased from Acros Organics. Pluronic F127 (PEO$_{106}$-b-PPO$_{70}$-b-PEO$_{106}$) and F88 (PEO$_{109}$-b-PPO$_{41}$-b-PEO$_{109}$) were donated by BASF. Silicon substrates (0.001-0.005 ohm-cm, p-type boron doped, <1-0-0>, 250-300 µm thickness and 50.8 cm in diameter) were purchased from Wafer World, Inc. Coleman grade carbon dioxide was purchased from Airgas. Aluminum pellets (99.99%) were purchased from Kurt J. Lesker.

3.2.2 Synthesis of acryloisobutyl POSS-co-AA copolymer

Atom transfer radical polymerization was performed to synthesize the ACPOSS-PAA copolymers.$^{49}$ Monomers of acryloisobutyl POSS and tert-butyl acrylate were first dried and purified. ACPOSS was dried under vacuum overnight, and tBA was washed with a solution of 5% NaOH and stirred it with Na$_2$SO$_4$. The solution was then distilled to remove the inhibitor and dried with CaH$_2$. tBA (8 gr), ACPOSS (8 gr), CuBr$_2$ (100 mg), CuBr (8 mg), Ebib (103 µl) and PMDETA (148 µl) were dissolved and mixed in 20 mL of toluene. The solution was then heated to 65 ºC. The polymerization was run for 48 hours, before the solution was run through silica gel to remove the copper bromide catalysts. The solution was then dried and analyzed. The deprotection of the tBA group to acrylic acid was done in 200 mL of trifluoroacetic acid and dichloromethane (60:40 weight ratio) solution for 24 hrs. The sample was dried
by blowing nitrogen through the flask. The copolymer changed from a very viscous, clear liquid to a white solid.

3.2.3 Synthesis of silica films in supercritical CO₂

The synthesis of silica in supercritical CO₂ was outlined previously.²¹ In this study, we first spin-coated a sacrificial polymer template onto a silicon wafer. The sacrificial polymer template for the work described here is comprised of Pluronic F127, POSS-PAA copolymers, and pTSA as the organic acid. These components were first dissolved into a mixture of toluene and ethanol (1:1 weight ratio). The 20 wt% solution were then filtered with 0.45 µm PTFE membrane, and then spin-coated onto silicon substrate under a dry nitrogen condition at 2000 RPM. The resulting thicknesses of the polymer films are in the order of ~1 µm.

The film was then loaded into a high-pressure reactor and heated to 60 °C. About 8 µl, depending on the film mass, of TEOS and/or MTES precursors and 0.2 ml of water were preloaded into the reactor. Overloading the precursor amount can lead to surface deposition indicated by a white opaque layer on top of the deposited films. This introduces roughness to the films that would prevent optical analysis and large uncertainties in the thickness measurements of the films.

The vessel was sealed and equilibrated to reaction temperature, monitoring the vessel through the gas-phase thermocouple. A syringe pump (ISCO 500D Teledyne ISCO, Inc) was used to pressurize the reactor with a linear pressure ramp over 90 minutes to a target pressure of 124 bar. The pressure was held for another 30 minutes before the overnight depressurization. After the reaction, the film was calcined to remove the organic polymer template at 400 °C with ramp
up, soak and ramp down times of 4, 6 and 4 hours. Finally, The films were removed for analysis.

3.2.4 Capacitance Measurement

An accurate measurement of capacitance is the key to obtaining the dielectric constant of the silica insulator layer. In order to calculate $k$, the capacitance has to be measured across the oxide layer. Because the low-k films were synthesized on a silicon wafer, a parallel-plate capacitor model was utilized to do the measurement. Ideally, the parallel-plate capacitor measurement is done on metal-insulator-metal setup, which means that the insulator film is sandwiched between two metal contacts. However, due to the substrate limitation, a metal-insulator-semiconductor (MIS) setup is utilized in this work. A low-resistivity silicon substrate became necessary to reduce errors in the measurements. Figure 3.1 is an illustration of the MIS basic configuration. The semiconductor substrate used in the measurement requires DC bias voltage across the substrate and film to reduce the resistance of the substrate. The measured capacitance across a semiconductor substrate depends on the bias voltage applied. Figure 3.2 illustrates a typical C-V curve for a p-type semiconductor. The curve has distinct three-region characteristics, accumulation, depletion, and inversion. In a p-type semiconductor, the charge travels across the substrate through the presence of holes. A negative bias causes the charge carrier to accumulate at the semiconductor substrate/oxide interface. As the voltage rises toward positive, the charge carriers start to move away from the interface, and a layer of insulator forms, thus forming a second capacitor in series. The net result is a decreasing
measured capacitance. At the inversion, most holes are already in the inversion layer; thus, the measured capacitance reaches a flat inversion state.

Parallel capacitance model was utilized in the measurement of the dielectric constant of the oxide layer. The dielectric constant can be calculated from the capacitance measurement through the following equation:

$$ k = \frac{C d}{\varepsilon_0 A} \quad (3.1) $$

where $C$ is the capacitance, $d$ is the thickness of the oxide film, $\varepsilon_0$ is the vacuum permittivity, and $A$ is the area of the metal contact. AC signal was utilized to measure the capacitance of the oxide layer. The measurement of capacitance was done assuming simple RC circuit in series. The generalized Ohm’s law states that the impedance of the circuit can be calculated by dividing the voltage by the current. The impedance in this case contains the resistance and the capacitance in the circuit. The resistance part of the impedance does not alter the phase between the source voltage and the resulting current, while the capacitance part makes the voltage lead the current by -$\pi$/2. During the measurement, this phase difference between the current and voltage is monitored to be within 1% of -$\pi$/2 radian.

The capacitance measurement was performed using a metal-insulator-semiconductor setup with films synthesized on p-type low-resistivity silicon wafers. Aluminum contacts were deposited on top of the silica films using e-beam evaporator (SE-600, CHA Industries, with cryopump) through a shadow mask of three different nominal diameters (1, 1.5 and 2 mm). There are some variations in the actual area of the deposited metals compared to the nominal area of the shadow mask. This variation in area significantly affected the dielectric constant.
calculations. Thus, the actual metal contact areas were measured with optical microscope and ImageJ analysis software (National Institutes of Health). Metal contact deposition through a wet lithography technique was also explored. The resulting metal contact was very accurate and uniform; however, there was an oxide-delamination problem from the harsh lithography process. A sweep of bias voltage between -60 V to 0 V was applied during the measurement with 30 mV and 100 kHz in AC signal (Keithley Instrument 4200-SCS and Wentworth MP-2300 Probe Station). Negative bias was used due to the p-type substrate choice, and the measurement was conducted during the accumulation part of the capacitance. The thicknesses of the films were measured with profilometer (Dektak 150), right next to the tested pads. The actual areas of the pads were measured using optical microscope (Olympus BX51).

3.2.5 Nanoindentation

Nanoindentation is a simple test method to measure the mechanical properties of unknown materials. This measurement is conducted by indenting unknown samples using sharp-tipped materials with well-defined properties. The mechanical properties such as elastic modulus and hardness can then be calculated from the response of the samples during the indents. Recently, nanoindentation has become one of the most widely-used mechanical testing methods for characterizing thin films, especially in the microelectronic industry. This testing allows for high throughput measurement of mechanical properties while only requiring the materials to have a thickness greater than 1 µm.
This method relies on testing the material using a sharp tip to pierce the material, while making the distance travelled relatively shallow. The tip is usually made out of hard materials, typically diamond, to ensure no plastic deformation of the tip and a relatively accurate calculation of the hardness and modulus of the materials. The hardness and modulus are calculated from one indent profile. The nanoindenter provides a very sharp tip with a small force. Two parameters of the nanoindentation process were measured in nanoindentation, the force of the tip and the distance travelled into the films. Figure 3.3 shows a typical load-displacement curve from nanoindentation for a quasi-static experiment.

The hardness of the materials is calculated through as the maximum load divided by the contact area:

\[ H = \frac{P}{A} \]  

(3.2)

where \( H \) is the hardness of the materials, \( P \) is the maximum load exerted by the tip to the materials, and \( A \) is the projected area of the indenter tip into the materials. The elastic modulus of the materials can be calculated through the following equation:

\[ E_r = \frac{1}{\beta} \frac{\sqrt{\pi} S}{2 \sqrt{A}} \]  

(3.3)

where \( E_r \) is the reduced modulus, \( \beta \) is the geometry correction factor, \( A \) is the area and \( S \) is the stiffness, which is calculated as the slope of the load-displacement curve upon elastic unloading.
The calculation of material properties in the indentation experiment depends on the geometry of the indenter tip, mainly for the calculation of the projected area and the structure factor. The nanoindenter used in our experiment employs a Berkovich tip made from diamond. An ideal Berkovich tip has a predictable area as a function of the indent depth, and it has a geometry correction factor of approximately 1. \( \beta \) could vary slightly depending on the tip condition.\(^{50}\)

The projected area of an actual tip, however, most likely does not follow the ideal area-depth function: It could vary slightly from defect and wear from indentations. The film thickness and depth of indentation during the nanoindentation can affect the experimental results. In order to avoid the substrate effect, the indentation depth can only be in the range of 10-25% of the film thickness.\(^{51}\)

Silica film’s mechanical performance was characterized using quasi-static nanoindentation (TriboIndenter TI 900), with a diamond Berkovich tip. The films tested were at least 1 \( \mu \)m in thickness to minimize the substrate effect. The indentation test were done through load control with maximum load between 100-150 \( \mu \)N and ramp up, holding and ramp down times of 5, 5 and 5 seconds. Sixteen indents were performed on each sample.

3.2.6 Ellipsometry

Spectroscopic ellipsometry (GES-5 spectroscopic ellipsometer, SOPRA) was performed to measure the thickness and porosity of silica films. Incidence angle and reflection of 75\(^\circ\), the Brewster angle of silicon, and a wavelength of 300-800 nm were used in the measurement. The simulation and regression were
performed on WINELLI software. Bruggeman’s effective medium approximation was used in the simulation assuming the mixing of SiO₂ and void. Levenberg-Marquardt was used as the regression method.

3.2.7 Small Angle X-ray Scattering

The small angle x-ray scattering in this work was done on Rigaku-Molecular Metrology SAXS equipment at the W.M. Keck Nanostructures Laboratory. Samples were prepared from concentrated solutions of the polymer and polymer mixtures in ethanol and a small amount of water. The samples were then drop-casted onto a 1 mm thick washer, sandwiched between two Kapton® films. Afterward the drop-cast the samples were dried at 80 °C under vacuum overnight. The top Kapton® film was then glued onto the washer to keep polymer melts from flowing out of the holder. The data collection was done at 80 °C to make sure that the samples were at melt state. All data were collected at constant time (45 minutes) to ensure quantitative comparisons between spectra.

3.3 Results and Discussion

3.3.1 Mechanical Enhancement with POSS

The supercritical CO₂-infusion synthesis process relies on the acid catalyzed condensation of silicate or organosilicate precursor in a polymer matrix. This condensation process can be selective into one region of the microphase-segregated block copolymer when the acid segregates to the hydrophilic region of the block copolymer, leaving the hydrophobic region as the pore generator. One such BCP that can create small pores and is suitable with the process are the triblock copolymers of PEO-b-PPO-b-PEO (Pluronic by BASF). Since the
blending of two materials-- in this work POSS and Pluronic BCP---depends strongly on the solubility and compatibility of the two materials, a modification to the materials was necessary to induce compatibility. For our particular application, the inclusion of POSS into the polymer matrix can be problematic, mainly due to the POSS aggregation, which can significantly alter the film uniformity. Aggregation of POSS in polymer matrix, due to the incompatibility of the POSS and Pluronic BCPs, is the primary challenge of integrating POSS into silica films. Figure 3.4 shows the optical and AFM images of trisilanol isobutyl POSS blended with Pluronic F108. The AFM shows large cluster formations due to the incompatibility of the POSS and Pluronic BCP. Depending on the polymer and side-chain decoration of the POSS molecules, the aggregation can reach sizes up to several tens of micron in particle size, making it unsuitable to the semiconductor integration. The compatibility between POSS and its side groups dictates how the molecules can be dispersed in the polymer matrix. Most POSS-polymer composites utilize more hydrophobic polymers, which are compatible with the alkyl chains of the POSS. Even with hydrophobic polymers, one must choose POSS molecules to disperse well into the macroscopic composite.

We have recently shown that the blending of two polymers can be enhanced by the hydrogen bonds between the PEO and polymers with an acid group such as poly acrylic acid. Other groups have shown that by copolymerizing acrylic acid with polystyrene, the copolymer was capable of forming a miscible blend with the PEO. In fact, they found that the poly (AA-co-styrene) forms miscible blend with PEO at an AA concentration as low as 7
mol% in poly(AA-co-styrene). By copolymerizing acrylate monomers with a POSS side group (acryloisobutyl POSS (ACPOSS), Figure 3.5), one can induce the dispersion of these POSS molecules into the Pluronic BCPs. Strong interaction due to hydrogen bonding between the acrylic acid and the PEO would allow the POSS dispersion into the relatively more hydrophilic polymers.

The POSS-PAA copolymers were synthesized in the batch ATRP reaction with both monomers of tBA and ACPOSS. The molecular weight of the protected polymer was 13.9 kg/mol and PDI 1.26, which were measured by GPC using polystyrene standards. Figure 3.6 is the GPC result of the POSS-PtBA copolymers. The figure shows that there is one unimodal peak, indicating a single molecular weight distribution, while there is a small second peak that can be attributed to the unreacted POSS monomer. The NMR shows that the ratio of the synthesized polymers was very close to the feed ratio of tBA and ACPOSS at 2 to 3 mass ratio, which corresponded to 1 to 2.7 of PAA to ACPOSS mass ratio after the deprotection of the tert-butyl acrylate group (Figure 3.7(a)).\textsuperscript{57, 58} The difference between the feed ratio and resulting ratio can be attributed to the loss of unreacted tBA during the drying process. The comparison of mass ratio was performed by comparing the methyl singlet of the tert-butyl group in the tBA at \textasciitilde 1.45 ppm and the methyl doublet of the isobutyl group of the ACPOSS at 0.95 ppm. After the deprotection, the solubility of the copolymer changed from being soluble in a non-polar solvent such as toluene and chloroform, to being soluble in either THF or mixed non-polar and polar solvents such as a mixture of toluene and ethanol. The deprotection of the tBA group was also shown with the loss of
the tBA peak in the deprotected copolymer NMR spectra (Figure 3.7(a) and (b)). The deprotected copolymer was not soluble in polar solvent such as ethanol and other alcohols. Figure 3.7(c) shows the NMR spectra and peak assignment of the ACPOSS monomer.\textsuperscript{58}

After the deprotection step, blends of POSS and Pluronic BCP were analyzed to study the interaction between the POSS-PAA copolymer and the Pluronic BCP. The blended POSS-Pluronic blends were optically clear, and the spincoated films were uniform and clear as well. The interactions between POSS-PAA copolymer and the Pluronic BCP were characterized using SAXS. Figure 3.8 shows the SAXS spectra of POSS-PAA and Pluronic F127 blends. The spectra show clear interaction between the POSS-PAA and the Pluronic. The appearance of the first order peak indicates there is a strong segregation of the block copolymer due to the interaction of the two polymers. The second-order peak indicates a longer range correlation of the observed phase segregation. Primary and secondary reflection peaks of the scattering spectra were observed from 20 wt\% POSS-PAA concentration up to 40 wt\% POSS-PAA. The blending of POSS-PAA and F127 shifted the primary peak position from a broad peak of neat F127 at around $q=0.57 \text{ nm}^{-1}$ smaller $q$ at around 0.43 nm$^{-1}$. Neat POSS-PAA copolymer did not show any scattering correlation peak, indicating that the POSS-PAA copolymer induced the phase segregation of the Pluronic BCP due to the interaction of both copolymers. At 50 wt\%, the intensity of the primary peak of the SAXS decreased significantly, indicating disturbance in the phase segregation of the BCP blends. The disruption in the phase segregation was not observed on
PEO majority block copolymers, but such disruption was observed on PPO majority BCP at higher PAA loading. The disruption of the order in this case may be related to the POSS side groups containing isobutyl groups, which would preferentially segregate into the more hydrophobic domain. Similar trend was observed with the SAXS spectra of F108 and POSS-PAA copolymer blends.

The blending of Pluronic and POSS-PAA copolymers also affects the crystallinity of the PEO chain in the BCP. Figure 3.9 shows the DSC of the pure F127 and its blends with POSS-PAA. The decrease in the peak area of the DSC melting curve indicates the decrease in the crystallinity of the PEO when blended with POSS-PAA. There were significant decreases in the peak areas as the concentration of the POSS-PAA copolymers were increased. At 40 wt% POSS-PAA loading, the crystallinity of the PEO chain was completely suppressed.

The silica films synthesized using POSS-PAA and Pluronic blends as the template showed a significant improvement in mechanical properties. The POSS-PAA concentrations in the polymer templates were varied, while the other synthesis parameters were kept constant, to measure the effect of POSS-PAA on the mechanical properties of the silica films. Figure 3.10 summarizes the hardness and reduced modulus of the silica films synthesized from the POSS-PAA copolymer and F88 template and TEOS as the precursor. The POSS-PAA templated films showed a systematic increase in both hardness and modulus over a small range of porosity. The control film, templated from F88-PAA blend, had a slightly-higher hardness and modulus compared to the 10% and 20% POSS-PAA loadings. This decrease in mechanical properties at lower POSS-PAA loadings
could be attributed to the lack of a highly-ordered porous structure compared to the films synthesized with the F88-PAA blend. The F88-PAA-templated film showed well-ordered structure, while none of the POSS-PAA template exhibited strong enough correlation peaks on the small-angle XRD.

At higher POSS-PAA loadings, 30% and 40%, the porosity of the films were held relatively constant, a significant improvement in hardness and modulus were observed, with 40% of the POSS-PAA loading having a hardness of 900 MPa and reduced modulus of 10.8 GPa. A significant improvement in hardness and modulus was observed as the POSS-PAA was increased to 50%. Although the porosity decreased to 32.5%, from around 44%, the film hardness doubled from 900 MPa to 1.79 GPa, while the modulus increased to 31.7 GPa. This hardness was comparably higher than the previous study, where the hardness reached 1.0 GPa at k of 3.0.

The isobutyl side-group on the ACPOSS monomer is considered relatively hydrophobic. Depending on the survivability of the side group in the calcinations step, the side chain could act as the pore generator or hydrophobic group for the low-k film. The organic groups from organosilicate precursors have previously been shown to survive the calcinations process. Infrared spectroscopy shows that there was no observable peak from the isobutyl side chain of the POSS on the film.

For the low-k films, the MTES precursor was mixed with TEOS to increase the film hydrophobicity, while still preserving the mechanical integrity through complete silica bonds of TEOS. Other organosilicate precursors had also
been investigated for the scCO$_2$ process. The POSS-PAA-templated films also showed similar benefits on the mechanical performance of the films. The MTES-TEOS precursor mixtures had a better mechanical performance compared to porous silica films. Figure 3.11 outlines the family of MTES-TEOS films synthesized with POSS-PAA/F127 as the template compared to the MTES-TEOS films in the previous study. The hardness and dielectric constant results from the POSS-PAA followed the trend observed in the TEOS based films. The increase in hardness and modulus was achieved at a dielectric constant between 2.1 and 2.2 for POSS-PAA concentration up to 40%. At low POSS-PAA concentrations (10% and 20%) the improvement in mechanical performance was not observable. However, as the POSS loading was increased to 30% and 40%, a significant gain in the hardness was achieved: The hardness at k of 2.1 increased from around 800 MPa to more than 1.2 MPa with a slight increase in the dielectric constant. By varying the process condition, a slightly higher k was achieved at the same 40% POSS loading, while increasing the hardness of the film also increased similarly as the control. At 50% POSS-PAA content in the template, the film hardness jumped to just below 1.8 GPa, although the dielectric constant of the film increased to 2.4.

The porosity generated by the BCP template was an important aspect of the porous silica for dielectric barrier layer. In previous studies in our group, the pores were generated by the hydrophobic part of the BCP as well as the space occupied by the polymer matrix. The mesopores, generated by the BCP, follows
the preformed BCP, while the micropores represent the space occupied by the polymers before the calcination process.

The presence of POSS dispersed in the template, changed the morphologies of the silica films when compared to films templated by neat Pluronic BCPs. The resulting silica films showed the lack of a highly-ordered morphology in contrast to the order structure demonstrated silica films synthesized by Pluronic and Pluronic/PAA blends. The XRD spectra of films synthesized with POSS/PAA copolymer blended with Pluronic F127 and F108 did not show any Bragg’s diffraction correlation peak. Figure 3.12 shows the TEM image of silica film synthesized with the POSS/PAA and Pluronic F108 blends as the template. The TEM image shows continuous pores, different from the more isolated pore structure of the non-POSS films. The continuous pores could be caused by the presence of side chain of the POSS, occupying the space between the BCPs’ hydrophobic chains. Furthermore, the FT-IR study of the POSS films synthesized with straight TEOS (Figure 3.13) did not show any presence of alkyl chain after calcination, as observed on the organosilicate films. The lack of peak in the 2900 cm\(^{-1}\) region, characteristic of aliphatic C-H stretching vibration mode,\(^{61}\) suggests that, in contrast with organosilicate precursors, the side chains of the POSS molecules did not survive the calcination process, in contrast with organosilicate precursors.\(^{48}\)

3.3.2 Patterned Silica on Directed-Assembly BCPs

Our collaborator provided pre-assembled block copolymer, which was aligned through the directed assembly route. The PS-b-PtBA (3:7 weight ratio)
was spincoated onto a previously-patterned mono layer. The preferential wetting of each block of the BCP to the hydrophilic, hydrophobically-patterned surface guided the BCPs forming the device-level pattern. Figure 3.14 (a) and (b) show the aligned film and as-infused film. Comparing the aligned template film to the as-infused film, we found that the scCO₂ process did not affect the alignment of the block copolymer to the substrate.

The calcined films showed that the silica was deposited into the block copolymers. The underlying monolayer of hydroxy-terminated Poly(methyl methacrylate) was thin enough to allow the silica to anchor to the silicon wafer. Previous studies on the infusion of PMMA did not show any appreciable deposition. Figure 3.14 (b) and (c) show the as infused and calcined films, aligned with the underlying pattern. The bright phase of the SEM in the aligned and as-infused samples represent the PS phase of the BCP, while the darker region represents the PtBA phase. The infusion process of the film did not disturb the alignment of the BCP pattern. However, the calcined samples showed somewhat unexpected results from the as-spun/infused pattern. The calcined film shows line broadening of the pattern in contrast to the underlying pattern on the PMMA monolayer. This mismatch could be explained by the fact that the cylinders forming BCP was used in the template, which allowed the silica precursor to condense underneath the PS cylinders. The gap between the silica represents the contact of the PS to the underlying layer.

Further study of this process should be conducted using lamellar morphology BCPs, which would show whether the interface between the
hydrophobic phase of the BCP and the substrate could prevent the creeping of silica condensation into the hydrophobic region.

### 3.4 Conclusion

The blending of POSS into silica films synthesized in scCO₂ enhanced the hardness and modulus of the films. The incorporation of POSS into both silicate and organosilicate films allowed the synthesis of low dielectric constant films with higher mechanical performance compared to the control scCO₂ films. The scCO₂ synthesis method allowed for uniform incorporation of POSS in the silica films. The separation of template formation and condensation meant that the pre-dispersed POSS could be incorporated into the template, thus allowing the POSS to be uniformly distributed into the silica film. The dispersion of POSS into the hydrophilic block copolymer template was induced by the copolymerizing of POSS monomers and acrylic acid. Hydrogen bonding between acrylic acid and the PEO chain of the template increased the compatibility of POSS into the PEO-b-PPO-b-PEO triblock copolymer templates.

This study looked at the cylindrical morphology BCP, yielding in line-broadening of the pattern, relative to the underlying monolayer patterns. We also conducted a feasibility study into combining the directed assembly of BCP with the scCO₂-infusion method. Infusing the silica precursor into the BCP took advantage of the separation of BCP, which yielded a non-trivial silica pattern.
Figure 3.1. Metal-insulator-semiconductor basic set-up for capacitance measurement
Figure 3.2. A typical MOS capacitance measurement curve, constructed from measuring the capacitance of a CVD deposition of silica film on a low-resistivity p-type silicon wafer. The graph shows the area of accumulation, depletion, and inversion depending on the bias voltage.
Figure 3.3. A typical load-displacement curve of a nanoindentation experiment, where the hardness is calculated through the maximum load and indentation area and modulus is calculated from the slope of receding curve.
Figure 3.4. Optical and AFM images of a film of F108 blended with trisilanol isobutyl POSS at 10 wt %. The images show the aggregation of POSS inside the polymer matrix.
Figure 3.5. Acryloisobutyl POSS structure. It is an acrylate monomer with POSS as the side group. Isobutyl side chains are attached to the POSS cage.

R=isobutyl
Figure 3.6. GPC of acryloisobutyl POSS-PtBA copolymer indicating a molecular weight of 13.9 kg/mol and PDI of 1.26.
Figure 3.7. NMR spectra of (a) copolymer of acryloisobutyl POSS and tert-butyl acrylate. It shows the peaks from both the POSS molecules and the tert-butyl acrylate. After the deprotection (b), the methyl peak from the tert-butyl group at 1.45 ppm disappeared. (c) is the NMR spectra of acryloisobutyl POSS monomer.
Figure 3.8. SAXS of Pluronic F127 and POSS-PAA blends indicating highly-ordered phase segregation of the BCP.
Figure 3.9. DSC of Pluronic F127 and POSS-PAA blends. The decrease in crystallinity and melting temperature of the PEO chain indicates the suppression of the crystal formation due to hydrogen bonding.
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Figure 3.14. SEM images of (a) aligned P(S-b-tBA) on silicon wafer, (b) infused template with TEOS, and (c) calcined silica after the infusion process.
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CHAPTER 4

SANS STUDY OF FORMATION AND BREAKING OF TERNARY SOLVENT/SOLVENT/SURFACTANT ORDERED ASSEMBLY INDUCED BY COMpressed CO₂

4.1 Introduction

Surfactant-stabilized solvent mixtures offer ready access to self-assembled structures for use as templates for materials and multiphase-reaction media. The differences in solvent/segment interactions and surface tension dictate the details of the structure and its robustness.¹⁻³ Many efforts have focused on the compatibility of the surfactant and the solvents. One particular co-solvent is compressed CO₂, which has the ability to dissolve small molecules and is easily tunable, while having lesser environmental impact than other volatile organic solvents. Being able to tune these interactions through the systematic variation in solvent quality (and differences in solvent quality) would enable easy access to structured solution and liquid crystals.

Nonionic surfactants such as the PEO-b-PPO-b-PEO and PE-b-PEO have been studied extensively for their structures at different surfactant concentrations and solvent compositions.⁴⁻¹⁷ The surfactants are capable of creating an oil-in-water emulsion at higher water-to-co-solvent ratio and water-in-oil at reverse concentration. These formations of water-in-oil and oil-in-water microemulsions are dictated by the ratio of the solvents with strong solubilization to the respective chains.¹³, ¹⁴, ¹⁸ The phase behavior of the ordered structures in liquid and liquid
crystals depends strongly on many factors, such as temperatures, co-solvent, electrolytes, etc. CO\textsubscript{2} can increase the compatibility of p-xylene with the PPO block and thus induce the formation of reverse micelles in PEO-b-PPO-b-PEO, water, and the p-xylene system.\textsuperscript{19-21}

In this study, we show that the formation of these ordered nanostructure solutions are controlled by the addition of compressed CO\textsubscript{2} into liquid and gel. While compressed CO\textsubscript{2} has been studied extensively in forming microemulsion to dissolve other solvents/materials,\textsuperscript{22-28} the effect of CO\textsubscript{2} on the two-solvent systems has not. Here, we utilized a small-angle neutron scattering technique to show the effect of CO\textsubscript{2} in the microphase separation of two solvents in the presence of surfactants. CO\textsubscript{2}-induced phase separations and formations of microemulsions were observed in systems with relatively lower surfactant concentration, while at higher surfactant concentration, the addition of CO\textsubscript{2} enhanced the long-range order of the phase segregated gels. The reverse effect can be achieved when the addition of CO\textsubscript{2} causes mixing of the solvent rather than demixing. The density, and thus the solvent strength of compressed carbon dioxide, can be precisely controlled through pressure mediation. At low pressure, compressed CO\textsubscript{2} is soluble in and will expand (up to 200 vol\% or more) in many organic and fluorocarbon solvents, including light hydrocarbons, light alcohols, acetone and others.\textsuperscript{29, 30} The concentration of CO\textsubscript{2} in the solvent dictates the solvent quality for the mixture. Thus, CO\textsubscript{2} is easily controlled by system pressure. At elevated pressures, single-phase CO\textsubscript{2}/solvent mixtures are accessible. By contrast, CO\textsubscript{2} exhibits very low solubility in water and in some other strongly
self-associating solvents such as methanol. In ternary CO₂/solvent/solvent systems, changing the pressure of CO₂ can (1) enhance miscibility of the solvents; for example, when both solvents are miscible with CO₂ but are incompatible with each other, and (2) decrease compatibility when the solvents are compatible, but one solvent is miscible with CO₂ while the other exhibits very low solubility in CO₂. At the extremes, there are numerous examples of CO₂-induced miscibility and CO₂-induced phase separation for solvent pairs.\textsuperscript{31}

4.2 Experimental

4.2.1 Chemicals

D₂O, d-methanol, acetone-d, and tetradecane were purchased from sigma Aldrich and used as received. The nonionic surfactants; Pluronic P105 was gratefully donated by BASF and Brij76 was purchased from sigma Aldrich. Both surfactants were used as received. The mixture of solvents and surfactant were stirred for 30 minutes on a hotplate at 60 °C before allowed to equilibrate in the pressure cell at experiment temperatures of 40 °C for another 30 minutes. After each addition of CO₂ to the experimental pressure, the samples were allowed to equilibrate for another 30 minutes.

4.2.2 Small-Angle Neutron Scattering (SANS)

The SANS data were collected on the NG7 30 m instrument at the National Institute of Standards and Technology\textsuperscript{32} with a neutron wavelength of \( \lambda = 6 \) Å at 25 °C. The detector was set at 4 m and allowed a scattering measurement with Q-range of \( Q = 4\pi\lambda^{-1}\sin(\theta/2) = 0.01 \) to 0.16 Å\(^{-1}\), where \( \theta \) is the scattering angle. The SANS data reduction was calculated with the data-reduction package
provided by the NIST Center for Neutron Research, utilizing IGOR Pro. The scattering spectra were corrected for the background using empty high-pressure cells with the sapphire windows. Then, we calculated the efficiency of the detector using the scattering from poly(methyl methacrylate) as an isotropic scatterer. The absolute intensity of the data was calculated by using the intensity of the direct transmission as the scaling factor.

The neutron-scattering experiment is based on similar scattering principles to the small-angle x-ray scattering discussed in chapter 2. The main difference between SANS and SAXS is the source of contrast in the materials. In SANS, the contrast between the components arises from the difference in the neutron scattering length. The cross section of the coherent neutron scattering practically follows the following equation:

\[
\frac{d\Sigma(q)}{d\Omega} = \sum_i \sum_j b_i b_j \exp \left( i \mathbf{q} \cdot \mathbf{r}_{ij} \right) \tag{4.1}
\]

where \( b \) is the scattering density of an element, \( q \) is the scattering vector, and \( r_{ij} \) is the vector between the elements. In order for this correlation to show in the detector, the scattering density contrast must be sufficient. One could use the group contribution method to calculate the scattering length density (SLD) of a material.\(^{33}\) Because neutron scattering relies on the scattering-length density of the studied materials, a larger contrast of SLD could largely be driven by the deuteration of the involved materials, mainly due to the large difference between the scattering lengths of hydrogen and deuterium (-0.37 and 0.67 \( \times 10^{-12} \) cm). Large differences in SLD help with the acquisition time of the SANS
experiments. In the coherent scattering of ordered materials, the periodic correlation distance between the two different SLDs gives rise to the Bragg reflections. The incoherent part of the scattering gives the non-zero background in the spectra.

The high-pressure cells were fabricated from stainless steel block with sapphire windows. The sapphire windows were secured through face seal with VITON® O-ring, which is inert to the organic solvent used in the experiments. To reduce the multiple coherent scattering from the strongly scattering samples, the path length of the samples needs to be kept as small as possible. The path length of the cell was set at 1 mm with the sapphire spacer in the cell. Stainless steel tubes from a syringe pump ((ISCO 500D Teledyne ISCO, Inc) delivered the compressed CO₂. Both the pressure cell stage and CO₂ were kept at experiment temperatures by a constant temperature- circulation bath. Digital pressure transducer was used to measure the CO₂ pressure. The sample pressures were measured immediately before the cell inlet and monitored them through the duration of the SANS data collection.

4.3 Results and Discussions

The solutions of the two solvents and the surfactant were investigated for the micelle formation and the strength of segregation through neutron scattering. Two systems were investigated: acetone and water with Pluronic P105 as the surfactant, and methanol and tetradecane with Brij76 as the surfactant. Figure 4.1 illustrates the two systems studied here: 1) CO₂-induced phase separation and formation of emulsion. 2) the phase mixing and emulsion breaking due to CO₂.
Acetone and water phase mix under ambient conditions, but upon the introduction of compressed CO₂, the two solvents phase-segregated. Conversely, methanol and tetradecane form different phases and phase mix with the presence of CO₂.³¹ The change in solubility of the two phases was utilized to affect the formation of micelle in the solutions.

4.3.1 CO₂-Induced Formation of Microemulsion

In solution, Pluronic surfactants form different structures depending on the surfactant concentration and co-solvents. At lower concentrations of surfactant in water or water majority solvent mixtures, the solution forms a clear liquid isotropic solution. However, at higher surfactant concentrations, the mixtures form gels with spherical, hexagonal, and lamellar morphologies.⁴ At lower concentrations, the formation of the microemulsions is dictated by the concentration of the surfactant and the compatibility of the solvents with the surfactant. For the amphiphilic surfactant, the selectivity of one surfactant block to the solvent can create a microemulsion with either a dry core, in which solvents are excluded from the core, or a wet core if the solution includes solvent that is preferential to the core materials.

The initial study for this work involved finding the concentration range in which microemulsions or ordered structures were formed at the different solvent ratio and surfactant concentrations in D₂O/acetone mixtures. Three different concentrations of Pluronic P105 were investigated: 10 wt%, 20 wt% and 30 wt% at three different ratios of D₂O to acetone. The solvent quality of the mixtures depended strongly on the ratio of the mixture. At higher concentration of acetone,
the polymer became highly soluble in the solution; at a lower acetone concentration, the polymer became less soluble. At the high concentration of PEO (20%) and a 7:3 D$_2$O-to-acetone ratio, the solution became very viscous, and at PEO concentration of 30%, the solution became gel-like. This is represented in the SANS spectra, which shows a highly-ordered system at a polymer concentration of 30%. Figure 4.2 shows the SANS spectra of acetone, D$_2$O, and P105 solutions at different concentrations and ambient conditions. The SANS spectra shows that at higher ratios of acetone to D$_2$O (8:2), no correlation peak was observed, indicating the solutions were disordered for all three different concentrations of P105. Weak peaks appeared at an acetone-to-D$_2$O ratio of 7:3 at 20 wt% and 30 wt% P105 concentrations, while the more pronounced and sharper peaks appeared at lower acetone-to-D$_2$O ratios of 4.5 to 5.5 and 3 to 7. These differences in phase segregation, and thus the sharpness of the scattering peaks, also follow the solubility trend. More viscous materials show sharper correlation peaks, mainly due to less mobility and better defined structure of the mixtures.

Table 4.1 summarizes the four solutions that were investigated further in the D$_2$O/acetone study. We chose two solutions with acetone majority and two solutions with D$_2$O majority; each had two different surfactant concentrations.

The solvent strength of acetone and water co-solvent at a given surfactant concentration determined the state of the mixture. At higher acetone majority samples, an acetone-to-water-ratio of 7:3 (Samples 1 and 2), the overall mixture was observed to be liquid-like. These solutions were then investigated with SANS to determine the microstructure of the mixture. Figure 4.3 shows the scattering...
spectra of the Sample 1 under CO₂ pressures ranging from 1.01 bar to 207 bar. The SANS spectra has been normalized so that the absolute intensity can be used as an indicator of the phase separation and the segregation strength of the two phases in the emulsion. A very weakly-segregated phase was observed in the SANS spectra before the introduction of CO₂ into the solution. D₂O and acetone was used to create neutron contrast for this experiment. The deuterization of water phase is more preferential due to the preferential segregation of CO₂ into acetone. As the CO₂ pressure increased, the primary correlation peak increased in intensity, indicating stronger segregation of the microemulsion. This increase, however, slowed down beyond a pressure of 111 bar. The peak position of the primary peak, which is inversely-correlated to the center-to-center distance of the structure, decreased only slightly from atmospheric pressure to higher pressure. However, this increase was slight and we can attribute it to the dilation of acetone by the CO₂ in the majority domain.

By increasing the concentration of surfactant from 30 wt% to 40 wt%, the primary peak at atmospheric pressure became slightly stronger than the initial peak of the 30 wt% surfactant concentration. Figure 4.4 shows the SANS spectra of Sample 2, as it was pressurized with CO₂. With the CO₂ pressurization in the emulsion system, the stronger peak appears similar to the 30 wt% surfactant concentration. However, the improvement in the microstructure of the microemulsion continued until we reached our highest experimental pressure at 213 bar. We can attribute this to the increase in the surfactant concentration, which allowed the solution to stabilize and contain the stronger phase separation.
of the solution. The phase diagram of acetone-water and CO$_2$ indicates that the solubilized water in the acetone phase depends on the CO$_2$ concentration/pressure. This change in water concentration allows for the variation in the segregation strength as observed on the SANS spectra. At 60 wt% surfactant concentration (not shown), the addition of CO$_2$ does not affect the scattering intensity and peak position of the sample up to 207 bar. The peak position of the microemulsion only changes slightly as a function of system pressure. We could attribute the slight decrease in the peak position to the increase in the center-to-center distance of the microemulsion resulting from the increase in the continuous phase of the emulsion. However, the increase is limited because of the change of the continuous phase does not significantly alter the emulsion size.

By reversing the solvent’s water-to-acetone ratio, the solubility of Pluronic in the solvents was also affected. At a low concentration (15 wt%, Sample 3), a broad primary peak, corresponding to an isotropic microemulsion was observed. The water and acetone at this condition, however, was thermodynamically phase-mixed. Before the introduction of CO$_2$, both solvents were expected to segregate into the PEO domain of the surfactant due to their affinity to the PEO, leaving the PPO core “dry.” The SANS spectra are shown on Figure 4.5. The increase in the scattering intensity of the primary peak indicates the increase in phase segregation of the solvents, induced by the presence of compressed CO$_2$. The scattering intensity increased significantly from 1.01 bar to 138 bar, and tapered off in absolute intensity up to the highest experimental pressure of 207 bar. This trend of intensity change in the primary scattering peak correlates closely with the change
in the peak position. The decrease of the position in the q-space indicates the increase in the center-to-center distance of the micelle, as the q vector inversely related to the d-spacing of the micelles. The increase in the d-spacing of the micelles, combined with higher scattering intensity of the spectra, can be attributed to the wetting of the previously-dry core of the emulsion. The change in the contrast between the D₂O-rich continuous phase and the acetone-CO₂ phase contributes to this change in the intensity. It can be argued that the increase in the d-spacing of the microemulsions was the result of the dilution by the CO₂.¹⁰ This change due to dilution, however, was followed by the decrease in intensity and broadening of the primary peak. The phenomenon was not observed in this CO₂-induced phase segregation.

Figure 4.6 shows the formation of ordered structure Sample 4 and the change to the structure upon the pressurization with CO₂ into the mixture. The appearance of second and third-order peaks as the pressure increases from ambient to 173 bar suggests that the addition of CO₂ increases the segregation strength between the two solvents. Starting from a CO₂ pressure of 110 bar, the emulsion exhibited a long-range order as observed with the appearance of the second and third order. The higher order peak is expected as CO₂ decreases the miscibility between acetone and D₂O. The high-order reflection peak also suggested that an order-to-order-transition occurred at 109 bar, as the ratio of higher-order peaks to the primary peak shifted from √3 to √4 and √7, indicating morphology transition between spheres to cylinders. The shifts in the peak position of the primary peaks indicated the change in the d-spacing of the
microemulsion. This increase indicated that the minority domain (acetone) was swelled by the addition of the CO₂ into the microemulsion.

The full-width-of-half-maximums of the acetone/D₂O solutions were also plotted as a function of the CO₂ pressure (Figure 4.7). There is a general trend of decrease in the FWHM as the CO₂ pressure increased. This decrease in the broadness of the primary scattering peak indicates that the phase-segregated structures inside the solution became more ordered with the addition of CO₂, in agreement with the increase in the peak intensity. However, Sample 4 did not so appreciably decrease in the FWHM. Still, from the appearance of higher-order scattering reflection peaks, we can deduce that the mixture also formed more-ordered structures as the CO₂ pressure was increased.

Figure 4.8 shows the change in d-spacing of the samples we studied, normalized to the d-spacing at ambient pressure. The observed increase in the domain sizes of the phase-separated structure follows the expansion of acetone/CO₂ expansion. Acetone experiences exponential increase in volume due to the addition of CO₂ as a function of pressure.²⁹ There are two general trends observed in this domain-spacing expansion: a rapid rise in the d-spacing, and the tapering off after a certain pressure (Samples 1 and 3), and the continuous increase in the d-spacing up to our highest experimental pressures (Samples 2 and 4). This difference in the expansion of the d-spacing can be attributed to limits on the formation of the emulsion through the difference in the available surfactants. As observed, Samples 1 and 3 have lower surfactant concentration when compared to Samples 2 and 4, respectively. This suggests that the expansion of
the acetone phase of the emulsion is limited by the concentration of surfactant in
the solution, where the surfactant can still form new emulsion with excess
available surfactant, thus slowing the growth in the d-spacing of the phase-
segregated structures.

Solvent selectivity of acetone-water mixture was studied by mixing d-
acetone and D\textsubscript{2}O and comparing the resulting scattering spectra with the acetone
and D\textsubscript{2}O mixture. Figure 4.9 shows that there was no significant difference
between the spectra of one or both solvents deuterated. The similarity between the
spectra suggests that the solvent before the addition of CO\textsubscript{2} selectively segregates
into one section of the surfactant. The similarity of scattering- length densities
between D\textsubscript{2}O (5.76 \times 10\textsuperscript{-6} Å\textsuperscript{-2}) and d-Acetone (4.9 \times 10\textsuperscript{-6} Å\textsuperscript{-2})\textsuperscript{33, 34} indicates that if
there was a phase segregation between the water and acetone in the mixture at
ambient condition, the correlation peaks would not have been observed due to the
lack of scattering contrast. More likely, the scattering contrast arises from the
“dry” surfactant core and the deuterated solvent mixtures. As observed in Figure
4.9, both the acetone majority and water-majority mixtures exhibit similar
behavior with limited difference between one and both deuterated solvents. The
slight difference might be explained by the change in the scattering length
densities between the d-acetone/D\textsubscript{2}O and acetone/D\textsubscript{2}O mixtures.

4.3.2 CO\textsubscript{2}-Induced Emulsion Breaking

Contrary to the formation of microemulsion discussed previously, CO\textsubscript{2} is
also capable in breaking a thermodynamically-stable microemulsion. The
breaking of microemulsion takes advantage of CO\textsubscript{2} ability to induce the phase
mixing of otherwise stable phase separated solvent pairs. Francis showed that CO₂ allows phase-segregated solvents to increase their compatibility as a function of the CO₂ concentration. There were hundreds of solvent pairs that exhibited such behavior. One such solvent pair that Francis investigated was methanol and dodecane. We chose tetradecane here, which has basic structure and solvent properties similar to those of dodecane, with Brij 76 as the surfactant.

Two different solutions were subjected to the SANS study. Both solutions exhibited stable microemulsion, forming clear liquid-like solutions at high concentrations of surfactant (37 wt% and 50 wt%). As the solutions were subjected to increasing CO₂ pressures, the intensities of the primary peaks of the spectra decreased. Figure 4.10a and Figure 4.10b show the SANS spectra of the Brij 76/d-methanol/tetradecane, as CO₂ pressures were varied. The two graphs represent the methanol majority (Figure 4.10a, d-methanol:tetradecane:Brij 76 ratio of 40:23:37) and tetradecane majority (Figure 4.10b, d-methanol:tetradecane:Brij 76 ratio of 20:30:50) solutions. Both solutions show disruption of the stable microemulsion formed by the components. Figure 4.10a shows that the change in the intensity of the scattering spectra did not occur before the CO₂ pressure reached 56 bar, while larger changes in the magnitude of the intensity started above 85 bar. The primary scattering peak disappeared completely at 138 bar.

Similar behavior was also observed with the tetradecane-rich solution. However, the pressure at which the scattering spectra were not observable was at
92 bar--lower than the previous system in study. Figure 4.10b shows the
tetradecane majority microemulsion.

4.4 Conclusions

Using compressed CO₂, we show that one can influence the formation of
microemulsions and lyotropic liquid crystal. The compressed CO₂ can
significantly alter the solubility of a two-solvent system. The change in solubility
works both ways, inducing phase separation and phase mixing, as one increases
the content of CO₂ in the solution. By using this solubility switch, we showed
that one can create or break microemulsion, as well as form highly ordered
lyotropic liquid crystal. The domain size of the microemulsion was also expanded
by the addition of CO₂ into the solution.
Table 4.1. Summary of CO₂-induced micro-phase separated solutions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>P105 (wt%)</th>
<th>Acetone (wt%)</th>
<th>D₂O (wt%)</th>
<th>Actone:D₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>49</td>
<td>21</td>
<td>7:3</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>42</td>
<td>18</td>
<td>7:3</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>26</td>
<td>59</td>
<td>3:7</td>
</tr>
<tr>
<td>4</td>
<td>35</td>
<td>19.5</td>
<td>45.5</td>
<td>3:7</td>
</tr>
</tbody>
</table>
Figure 4.1 Illustration of emulsion forming (a.) and emulsion breaking (b.) induced by compressed CO$_2$. The ability of the CO$_2$-induced emulsion to form relies on the phase separation of acetone and water due to the addition of CO$_2$, while the emulsion breaking relies on the phase mixing of methanol and tetradecane as a result of CO$_2$. 
Figure 4.2. SANS spectra of P105 at 10 wt%, 20 wt%, 30 wt% and a D2O-to-acetone ratio 0.2, 0.3, 0.7 and 0.8.
Figure 4.3. SANS spectra of P105-acetone-D$_2$O (30-49-21 weight ratio) as the sample was pressurized with CO$_2$. The intensity of the primary peak increased as the pressure increased, indicating better phase segregation between the acetone and D$_2$O. The increase in intensity slowed above 111 bar, while the peak position only decreased slightly between atmospheric and 207 bar.
Figure 4.4. SANS spectra of P105-acetone-D$_2$O (40-42-18 weight ratio) as the sample was pressurized with CO$_2$. This sample was acetone majority as of Sample 1, but at higher surfactant concentration. The intensity of the primary peak increased continuously as the pressure increased, indicating better phase separation between the acetone and D$_2$O. The peak position only decreased slightly between atmospheric and 215 bar.
Figure 4.5. SANS spectra of the water majority solution, P105-acetone-D$_2$O (15-26-59 weight ratio) as the sample was pressurized with CO$_2$. The sample showed strong segregation at ambient condition in addition to a strong increase in primary-peak intensity as the solution was pressurized. The increase in intensity tapered off above 111 bar, as did the peak position.
Figure 4.6. SANS spectra of water-majority solution, P105-acetone-D$_2$O (35-19.5-45.5 weight ratio) as the sample was pressurized with CO$_2$. The high surfactant and water concentrations allowed for the lyotropic liquid crystals to form. They were indicated by the appearance of sharp first-order peaks and the appearance of higher-order reflection peaks. At a CO$_2$ pressure above 109 bar, the ratio of higher-order reflection changed from $\sqrt{3}$ to $\sqrt{4}$ and $\sqrt{7}$, indicating order-to-order transition from spherical to cylindrical morphology.
Figure 4.7 Full width of half maximum of the four different acetone/D$_2$O solutions as functions of CO$_2$ pressure. The decrease of the FWHMs indicated stronger phase segregation between the acetone and D$_2$O.
Figure 4.8. A plot of the change in domain spacings of the four D₂O/acetone samples as a function of pressure, normalized to the d-spacings at ambient pressure. A general expansion trend of the domain spacings is consistent with the CO₂ driven acetone expansion.
Figure 4.9. SANS spectra of comparison between Acetone-d6/D2O and Acetone/D2O with the presence of P105 at the weight ratio of (a) Acetone:D2O:P105 of 21:49:30 and (b) 36:44:20
Figure 4.10. SANS spectra of d-methanol-tetradecane-Brij 76 (a. 40-23-37 weight ratio and b. 20-30-50 weight ratio) solutions as they were pressurized by CO₂. Both solutions showed the disappearance of correlation peaks indicating the disturbance of the formed structure.
4.5 References


CHAPTER 5

CONCLUSIONS

5.1 Conclusions

We studied the use of nonionic surfactant as the prearranged template to form highly-ordered structures. Pluronic triblock copolymer surfactant (PEO-b-PPO-b-PEO) is a family of versatile block copolymers that could form sub-10 nm micro-phase segregated morphologies. However, in melt, the segregation strength of the blocks is too small for spontaneous phase separation. Blending the Pluronic copolymers with hydrogen bonding homopolymer and poly (acrylic acid), allows the formation of long-range highly-ordered mesophase structures. The small-angle x-ray scattering study showed that the blending of Pluronic and PAA increased the apparent interaction parameters of the BCPs, which allowed for the Pluronic BCPs to phase segregate, forming sub-10 nm morphologies. This phase separation was utilized for practical applications: as templates for mesoporous silica, and formation of cobalt nanoparticles.

The hydrogen bonding between the PEO block of the Pluronic BCPs and acrylic acid was also used to induce the blending of PAA and POSS molecules. We polymerized acrylate monomers with POSS side groups with tert-butyl acrylate, which was deprotected into acrylic acid. We showed that the copolymerization of PAA with the POSS molecules interacted strongly with the Pluronic BCPs, overcoming the tendency of the BCP to form clusters in the relatively hydrophilic Pluronic BCPs. We showed that these two copolymers
became miscible as indicated by the suppression of crystallinity of the PEO chain, and that they induced phase segregation of the BCP as indicated by the SAXS spectra.

The incorporation of POSS into the polymer matrix was utilized to synthesize POSS-doped silica and organosilicate films for low-k dielectric barrier layers. This incorporation significantly enhances the mechanical properties of the barrier layer, improving the hardness and modulus at given dielectric numbers. This improvement was achieved through a one-step synthesis procedure, without further post treatment. We observed an increase in hardness to 1.8 GPa for an organosilicate film with k=2.4 and 1.2 GPa for k = 2.1. This improvement in mechanical robustness could be because of the POSS cage configuration having tetrahedral- bond geometry.

Finally, by using compressed CO₂, we showed that one can influence the formation of microemulsions and lyotropic liquid crystal. The compressed CO₂ can significantly alter the solubility of a two-solvent system. The change in solubility works both ways: as CO₂ content increases in a solution, it induces phase separation and phase mixing. We utilized this solubility switch to create microemulsion formation or breaking, to increase the segregation strength, and to alter the domain size of the microemulsions.

5.2 Future Work

We presented different approaches of combining the block copolymer and scCO₂ in the nanomaterial engineering. The work we present here can be divided into three different fields: sub-10 nm BCP morphologies through hydrogen
bonding, synthesis of increased mechanical performance low-k films utilizing the hydrogen bonding of polymers to incorporate POSS into the films, and utilizing compressed CO\textsubscript{2} to tune the formation of microemulsions and lyotropic liquid crystals in two-solvent surfactant systems.

The advantage of the hydrogen-bond homopolymer and BCPs investigated in Chapter 2 is the availability and low cost of the materials. This low cost allows for the high throughput manufacturing of sub-10 nm materials. One could imagine a roll-to-roll coating through the slot-die process to manufacture large surface area devices. These devices could include polymer-based solar cells, catalysts, and sensors\textsuperscript{1, 2}. The overall increase in surface area using BCPs as templates would provide increases in the overall performance of these devices. The research area would include the compatibility of dyes, sensors, and catalysts to be paired with the BCPs. Furthermore, the stability of the materials and overall degradation of the BCPs needs to be addressed, especially considering the crystallization of the PEO chains for the PEO majority and the mechanical robustness of the short-chained PPO majority of the Pluronic BCPs.

In Chapter 3, we showed how dispersing POSS into silica films increases mechanical performance. The direction of the research can be extended and apply to various block-copolymer patterning. The robustness of hydrogen bonding of the copolymers of POSS with PAA is a good candidate for the combination with other “bottom-up” approaches in silica patterning. The combination of directed assembly or direct patterning with POSS can achieve ULK for back-end-of-the line-application, by providing extra benefits of simplifying the synthesis steps,
while providing more robust materials than the current process. Furthermore, one can study the integration and dispersion of POSS into silica through the other synthesis routes, such as EISA and polysilicone-based ULK.\textsuperscript{3, 4}

Finally, we can extend the application of the compressed CO\textsubscript{2}-tuned microemulsion formation as a synthetic route for monolithic mesoporous materials. This synthetic route would provide advantages to the synthesis process by allowing one to use less-toxic, compatible solvents, like water and acetone.
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