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#### TITLE Impact of Dispersed Nanoparticles in Block Copolymer Soft Solids

PRESENTED BY Melissa Dao

ACCEPTED BY THE DEPARTMENT OF

Chemical Engineering

LYNN WALKER	4/25/16
LYNN WALKER, CO-ADVISOR	DATE
MICHAEL DOMACH	4/25/16
MICHAEL DOMACH, CO-ADVISOR	DATE
LORENZ BIEGLER	4/25/16
LORENZ BIEGLER, DEPARTMENT HEAD	DATE

APPROVED BY THE COLLEGE COUNCIL

VIJAYAKUMAR BHAGAVATULA

DEAN

### Impact of Dispersed Nanoparticles in Block Copolymer Soft Solids

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in

**Chemical Engineering** 

Melissa Ming-tsu Dao

B.S., Chemical Engineering, University of Washington

Carnegie Mellon University Pittsburgh, PA

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#### Abstract

Block copolymer soft solids are emerging as a means to spatially organize and store nanoparticulate material. Soft solids are formed as a disordered triblock copolymer solution  $[PEO_x-PPO_y-PEO_x]$  transitions to a lyotropic liquid crystal. For certain chain architectures, the crystal structure of the soft solid undergoes an order-order transition (OOT) from spherical micelles packed in a cubic crystal structure to close packed cylindrical micelles. The focus of this thesis is to determine the impact of processing conditions and formulation on the structural parameters, flow mechanism, and timescales of soft solids.

We study the effect of structural history and applied flow fields on the soft solids while the formulation is varied by incorporating nanoparticles into the polymer matrix. In the cubic phase, we found that the ordering kinetics occur on the timescale of minutes to tens of minutes depending on the structural history and the presence of particles. Furthermore, ordering of the cubic phase through the OOT occurs epitaxially. Without nanoparticles, a short application of high amplitude oscillations will macroscopically align the cubic and cylindrical phases into a persistent near single crystal. Changing the formulation through the addition of nanoparticles makes it more difficult to align the micellar crystals by shear, decreases the persistence of the alignment, and can change the unit cell of the micelle structure.

By varying the formulation and phase behavior of the polymer matrix, nanoparticles can access different types of flocculation behavior. Specifically, the particles will aggregate in both the liquid and soft solid, remain dispersed in both phases, or re-disperse upon formation of the soft solid. These findings provide additional design parameters to improve the templating of nanoparticles in the soft solid as well as highlight the feasibility of using the phase behavior of the polymer solution to control the flocculation behavior and aggregate size. Most importantly, the results in this work are crucial for effective processing of these composite systems and for development of future applications.

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#### **Chapter 1 Introduction**

Block copolymer melts and solutions are used as templates to direct the spatial organization of nanoparticulate material. Tunable arrangement of nanoparticles is vital for applications such as long-term nanoparticle storage and sensing devices as well as for the development of novel composite materials.<sup>1–6</sup> The properties of these composite materials are highly dependent on the spatial distribution of the particles, which is defined by both the separation distance between the particles and the shape and size of the three-dimensional assembled particle structure.<sup>7–13</sup>

The focus of this work is to use block copolymer soft solids, made from concentrated triblock copolymer  $[PEO_x-PPO_y-PEO_x]$  solutions, as a method to template, store, and segregate nanoparticulate materials. Prior work has characterized the structure and mechanics of many polymer systems<sup>13–20</sup>, and demonstrated the feasibility of templating nanoparticles in the solvent-swollen nanoscale structure.<sup>12,13,21–23</sup>

While these systems are capable of forming nanoparticle arrays, these materials are soft and deformable with the consistency of hair gel. Therefore, the nanoscale structure can be varied with small deformations. Understanding the impact of applied flow fields and added nanoparticles is vital for understanding processing and the further development of applications.<sup>6</sup> Previous work has shown that these systems form as a polycrystal that can be macroscopically aligned with an applied flow field and maintain that alignment.<sup>13,14,16,18,23</sup> Based on prior work, it is assumed that high shear rates, such as those accessible in

industrial manufacturing, will result in a persistent shear-aligned state.<sup>14,16</sup> The first goal of this thesis is to test this assumption by determining the impact of processing conditions and formulation on the shear alignment of the polymer template. The processing conditions examined are applied flow fields and thermal history while the formulation is changed by adding nanoparticles.

Chapter 2 provides background information about the structural features of block copolymer soft solid and templating of particles within the soft solid. Chapter 3 describes the materials and methods used to create the polymer-particle composites, and the scattering and rheological experimental techniques used to probe the structure and mechanics.

Chapter 4 examines the impact of applied shear and added protein on the flow mechanism and structural properties of soft solids. Two polymer systems are chosen that observe a temperature-induced order-order transition (OOT) from a cubic to a cylindrical phase which provides the ability to examine the impact of particles on different unit cell structures within a single system.<sup>18,24</sup> The nanoparticulate material added are globular proteins bovine serum albumin (BSA) and lysozyme. Rheology and small angle neutron scattering (SANS) with contrast variation determine the impact of protein and applied shear on the structure and mechanics of the soft solid. Without the added protein, the applied shear aligns the soft solid into a persistent single crystal. However, the added protein can make the system more difficult to align, decrease the persistence of the alignment, and generate a persistently aligned state that cannot be changed with shear.

In Chapters 5 and 6, the same composite systems are examined; however, the processing condition exploited is structural history. The dynamic relationship between structure and temperature provides the ability to examine the impact of structural history on the cubic phase of the soft solid. Structural history is varied by forming the cubic phase from a disordered liquid through the order-disorder transition (ODT) and from an aligned cylindrical phase through the OOT. Chapter 5 presents results for the neat polymer systems (without protein) while Chapter 6 presents results for the particle-polymer composite systems. The polycrystallinity, orientation, and ordering kinetics of the cubic phase depend on the structural history. Adding protein impacts the ordering kinetics and polycrystallinity of the cubic phase formed through the OOT but not through the ODT.

The final part of this thesis examines these composite systems from a colloidal perspective. Previous work used hydrophilic nanoparticles (electrostatically stabilized silica, sterically stabilized gold, lysozyme) that are stable in the liquid and soft solid phases of the polymer system.<sup>24,25</sup> BSA, which is electrostatically stabilized at this pH, showed regions of lower stability. The protein is observed to aggregate in the liquid and then re-disperse in the soft solid.<sup>25</sup> This re-dispersion highlights the need to better understand the impact of colloidal interactions on the stability or flocculation behavior of particles. Chapter 7 demonstrates the impact of steric, electrostatic, and depletion interactions on the stability of the particles. These interactions are tuned through the formulation of the system; this is done by varying the length of the stabilizing ligand on the nanoparticles, the ionic strength of the solvent, and the polymer concentration.

We observe three types of particle flocculation: stability in the liquid and soft solid, aggregation in both phases, or the re-dispersion in one phase. In addition to the ionic strength and length of stabilizing ligands, the flocculation behavior is also dependent on the structural features of the polymer template and the material properties of the particles.

The thesis demonstrates the feasibility of using the structural features of the soft solid to control the aggregation of nanoparticulate material and provides new design parameters required for successful particle templating or tunable aggregation. Furthermore, this work provides new insight on the impact of added particles on the processing of solvent-swollen micelle crystals, and highlights the need to understand the impact of processing conditions and formulation for proper handling and manufacturing of these materials. The findings presented are critical for further developing soft solids for applications that require a controlled arrangement of particles.

#### 1.1 Objectives

There are three primary objectives for this thesis. First, identify the effect of processing conditions (temperature, applied flow, and thermal history) on the structural parameters, flow mechanism, and ordering kinetics of block copolymer soft solids. Second, determine the impact of added nanoparticles on the processing of block copolymer soft solids. Third, evaluate the impact of colloidal interactions on the stability and aggregation behavior of nanoparticles dispersed in the polymer matrix to provide additional design parameters for successful templating.

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#### **Chapter 2 Background**

#### 2.1 Block copolymer template

Block copolymers swollen in a selective solvent self-assemble into nanostructured soft materials with solid-like macroscopic properties.<sup>1–4</sup> The soft solids considered in this work arise from the micellization of ABA block copolymers in solvents selective to the A block, which has been studied extensively over the last several decades.<sup>5–17</sup> At high polymer concentrations, the micelles organize into crystalline lattices, forming a soft solid with gel-like behavior.<sup>6,11,12,18–23</sup> These nanostructured polymeric soft materials are being used as templates for the development of materials with novel properties and applications such as long-term particle storage.<sup>24,25</sup>

The nanostructure of these soft materials depends on variables including polymer architecture, concentration, temperature, solvent quality, and additives such as nanoparticles or salts.<sup>5–7,14,19–23,26–31</sup> Typical morphologies observed are spherical micelles arranged in a cubic structure (face-centered cubic (FCC)<sup>20</sup>, body-centered cubic (BCC)<sup>5</sup>), hexagonally close packed cylindrical micelles (HEX)<sup>6</sup>, or a lamellar structure (LAM)<sup>18</sup>. Depending on the conditions, some soft solids go through order-order transitions, OOT, between different ordered structures. Order-order transitions have been observed between different cubic structures<sup>21,23,26,32</sup>, and cubic and cylindrical phases.<sup>14,23,33,34</sup>

Three structural parameters can be used to describe the nanostructure: the micelle morphology, the unit cell of the close packed micelle structure, and the polycrystallinity or defect structure of the system. When combined, these

structural parameters cover lengthscales that are on the order of nanometers to micrometers. The structural parameters are sensitive to processing conditions such as temperature, thermal history, and applied shear. Figure 2.1 illustrates the structural features at different lengthscales. At the nanometer lengthscale, the micelle morphology and unit cell structure respond to temperature and thermal history.<sup>6,14,23,26,33</sup> At the micron or larger lengthscale, the formed soft solid is initially polycrystalline or made of many micellar crystals separated by grain boundaries.<sup>6,15,35–37</sup> Applied shear can effectively align the micellar crystals into a single crystal, and depending on the mode of flow, the system will homogenously align throughout the gap or be shear-banded.<sup>5,9,10,38–40</sup>



Figure 2.1: Illustration of the structural features at different lengthscales.

The particular block copolymer soft solids of interest are made from concentrated solutions of the amphiphilic triblock copolymer known by the tradename Pluronic<sup>®</sup>, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) [PEO<sub>x</sub>-PPO<sub>y</sub>-PEO<sub>x</sub>], for which water is the selective solvent. At relatively low temperatures ( $\leq 5^{\circ}$ C), both PEO and PPO blocks are soluble in water.<sup>1,41</sup> As temperature increases, the PPO block becomes increasingly hydrophobic which

results in the self-assembly of micelles with a PPO core and a PEO corona. The high aggregation number of these micelles gives rise to hard sphere-like interactions in solution.<sup>6</sup> As the micelle volume fraction approaches the crystallization volume fraction, the micelles spontaneously organize into a lyotropic liquid crystalline phase. The phase behavior of many Pluronic<sup>®</sup> systems has been determined using a variety of techniques such as small angle scattering, birefringence and rheology. Depending on the formulation of the system, the soft solid may exhibit a temperature-induced OOT.

#### 2.2 Templating nanoparticles

Spatially organizing nanoparticles in block copolymer templates has been achieved through various methods. These approaches vary the particle size, shape, and compatibility with the polymer blocks to guide the nanoparticle distribution. As a result, particles will be sequestered to a specific polymer domain, the interface between two polymer domains, or defects such as grain boundaries.<sup>15,28–30,36</sup> The alternative strategy to adding particles is to synthesize particles within the polymer template.<sup>42</sup> While these methods have successes, they limit the scope of particles that can be used and may require additional surface modification of the particle.

The approach used in this work is one that has previously successfully templated hydrophilic nanoparticles in these Pluronic<sup>®</sup> soft solids.<sup>12,29,30,43–45</sup> The advantages of this method are its universality in templating pre-prepared hydrophilic nanoparticles and that it does not require extra particle modification.

This method utilizes the self-assembly of soft solid nanostructure to sequester the nanoparticles in the solvent-rich interstitial spaces located between the micelles.<sup>29,30,43</sup> This is achieved by dispersing the particles in the polymer solution at low temperatures where the system is a liquid. With increasing temperature, spontaneous self-assembly of the soft solid forces the nanoparticles into the interstitial spaces. The result is nanoparticle arrays templated in thermoreversible block copolymer soft solids. This method requires that the particles form a stable dispersion in an aqueous solution, the particle size be comparable to the size of the interstitial space (determined from scattering techniques), and the particle loading be  $\leq 1$  particle per interstitial space.<sup>29,44</sup> These guidelines are in place to ensure that the added particles do not overload or distort the polymer template.

Furthermore, the diffusivity of the particles within the soft solid proceeds via a hopping mechanism and is influenced by the polymer block length and concentration.<sup>17</sup> Polymer systems with micelles that have a thinner corona and larger corona are more efficient in "locking down" or decreasing particle diffusivity.<sup>17</sup>

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#### **Chapter 3 Materials and Methods**

#### 3.1 Block copolymer

Amphiphilic triblock copolymers known by the tradename Pluronic<sup>®</sup> [PEO<sub>x</sub>-PPO<sub>y</sub>-PEO<sub>x</sub>] area donated from BASF (Mount Olive, NJ) and used as received. Pluronic<sup>®</sup> is commercially available with varying molecular weight and block lengths. The polymers used in this work are Pluronic<sup>®</sup> F127, P123, and P103. In the naming convention, the letter describes the state in which the polymer is stored, where "F" is a flake and "P is a paste.<sup>1</sup> The first two numbers provide information about the PPO block length, and the last number indicates the weight fraction of the PEO content.<sup>1</sup> Table 3.1 summarizes the properties of the polymers used in this work.<sup>2,3</sup>

Pluronic®	Molecular	PEO repeat	PPO repeat	PEO wt%
	weight	units (x)	units (y)	
F127	12600 g/mol	106	70	70
P123	5750 g/mol	20	70	30
P103	4950 g/mol	16	60	30
		• • • • •		I

Table 3.1: Properties of Pluronic<sup>®</sup> used in this work.

The benefit of using Pluronic<sup>®</sup> is that there is an extensive amount of background on the phase behavior of these systems, it is FDA approved, and most importantly, it demonstrates reproducible behavior.<sup>1,4</sup> It is noted that Pluronic<sup>®</sup> obtained from the manufacturer does contain up to 25wt% impurities which are residual homopolymer and diblock copolymer formed during the synthesis.<sup>5,6</sup> However, the impurities do not impact the reproducibility of the phase behavior and soft solid structure. This reproducibility is particularly important because it shows that these polymers can be used as is without further purification.

#### 3.2 Nanoparticles

Based on previously determined templating requirements, nanoparticles used in this work are hydrophilic and similar in size to the interstitial spaces of the micellar crystals.<sup>7,8</sup> Both inorganic and organic nanoparticles are used in this work. All particles are roughly spherical in shape. The inorganic particles are Ludox SM silica nanoparticles that have a reported nominal diameter of 7nm and are obtained from Sigma Aldrich (St. Louis, MO).<sup>9</sup> The product is received as a 30wt% suspension at a pH of ~10 and used without further purification. In water (pH~7), the silica has a zeta potential of approximately -40mV. In addition to silica, synthesized gold nanoparticles (synthesis procedure in Section 7.2.1) with hydrodynamic diameter of ~7nm are used.

The organic nanoparticles used in this work are globular proteins that are chosen for their monodispersity, ideal size, and water solubility. The specific globular proteins are bovine serum albumin (BSA) that has not been defatted (product number A2153) and lysozyme from chicken egg white (product number L6876) obtained from Sigma Aldrich (St. Louis, MO) as lyophilized powders and used as received. The hydrodynamic diameter of BSA and lysozyme are ~7nm and ~4nm, respectively.<sup>10–12</sup> The isoelectric point (pI) of BSA is between 4.7 and 4.9 and the pI of lysozyme is 11.35.<sup>13,14</sup> At a neutral pH, the BSA and lysozyme have opposite charges, with BSA being negatively charged.

#### 3.3 Sample preparation

The samples are prepared according to this procedure unless otherwise specified.<sup>7</sup> The protein concentration is reported as a weight fraction of the total

sample while the polymer concentration is reported as the weight fraction in the polymer-water matrix.

Concentrated stock solutions (>40wt%) are prepared by dissolving Pluronic<sup>®</sup> in H<sub>2</sub>O (18M $\Omega$ ) or 99.9% deuterium oxide (D<sub>2</sub>O) obtained from Cambridge Isotopes. Dissolving the Pluronic<sup>®</sup> requires the samples to be refrigerated for up to seven days. These polymer stock solutions are used to prepare samples with varying H<sub>2</sub>O and D<sub>2</sub>O content.

To prepare neat polymer samples (without particles), the stock solution is diluted with H<sub>2</sub>O or D<sub>2</sub>O to achieve the desired concentration and solvent composition. The protein-polymer composite samples are prepared by initially dissolving the proteins in H<sub>2</sub>O or D<sub>2</sub>O. The necessary amount of polymer stock solution is then added to the protein dispersion. This addition is done at low temperatures where the solution is a viscous liquid (~5°C). The samples are mixed vigorously and allowed to equilibrate in the refrigerator (T~5°C) for up to a week.

For the bulk rheology, spectrophotometry, and x-ray scattering experiments, the solvent is water (H<sub>2</sub>O). For the Rheo-SANS experiments, contrast matching is used to isolate the scattering from the polymer phase. The scattering length density of the solvent is matched to the protein by varying the ratio of hydrogen (H<sub>2</sub>O) and deuterium (D<sub>2</sub>O). The protein-matched solvent is composed of 40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O and is the same for both BSA and lysozyme.<sup>15,16</sup> The systems without particles (neat) are also prepared with protein-matched conditions so that all of the scattering data has the same incoherent scattering background.

#### 3.4 Rheology

Rheometric experiments are performed on a stress-controlled DHR-2 rheometer (TA Instruments; New Castle, DE). Two types of geometries are used: a parallel plate geometry and a Couette cell. The parallel plate geometry has a gap of 800µm with a Peltier plate that controls the temperature of the bottom plate. The Couette cell has a cup I.D. of 30mm and a bob O.D. of 28mm for a 1mm gap. For all of the experiments, samples are loaded at as a liquid and allowed to thermally equilibrate at 5°C for at least 5 minutes to eliminate any loading and thermal history effects. Mineral oil is placed around the edge of the sample to prevent dehydration during the experiment.

Temperature sweeps are conducted using the parallel plate geometry to measure the thermal response of the system. The magnitude of the complex modulus (|G\*|) is measured as the system is heated and cooled between 5°C and 45°C using a fixed strain and frequency of 0.5% and 1rad/s that are verified to be in the linear regime. The linear regime is determined from amplitude sweeps conducted at 3-5°C increments between 5°C and 45°C. For example, for 35wt% P123 with 3wt% BSA, the protocol implemented conducts amplitude sweeps in a specific temperature sequence: 5°C, 7°C, 10°C, 14°C, 22°C, 35°C, 45°C, 40°C, 30°C, 25°C, 17°C, and 12°C. The sample is equilibrated at each temperature for 15 minutes, and between temperatures, the system is cooled to 5°C for 10 minutes to eliminate shear history.

The Couette cell is used for modulus relaxation experiments. This experiment measures the systems response to a structural transition and to applied shear. In this work, structural transitions are induced by temperature. The start of
the structural transition is defined as the time the temperature changes. Once the structural transition begins, the modulus is measured for 50 minutes with small amplitude oscillation (0.5%, 1rad/sec), after which high amplitude oscillatory shear is applied. The modulus after the cessation of shear is measured for 90 minutes using the same small amplitude oscillations.

### 3.5 Small angle scattering

Small angle neutron scattering (SANS) and small angle x-ray scattering (SAXS) are non-invasive techniques used to study the structure of materials on the order nanometers to microns. Figure 3.1 shows a schematic of the SANS and SAXS instruments. The neutrons or x-rays are generated from a source, which is either a nuclear reactor or a Cu K<sub> $\alpha$ </sub> radiation source, and are collimated to form an incident beam that is directed at the sample. A considerable amount of the incident beam is transmitted through the sample, some is absorbed by the sample, and the remainder is scattered by the sample.



Figure 3.1: Schematic of SANS and SAXS experiments.

Diffraction of the scattered beam is used to determine the degree of order in the system. The scattering intensity is a summation of coherent and incoherent scattering. Incoherent scattering is the background intensity that is measured at high scattering angles and subtracted from the scattering profile. The angular dependence, or q dependence, of the coherent scattering provides structural information about the system. The magnitude of q represents a wavelengthnormalized scattering angle given by Equation 3.1.

$$q = \left(\frac{4\pi}{\lambda}\right) \sin\left(\frac{\theta}{2}\right)$$
(3.1)

For a multicomponent system, such as the particle-polymer composites used in this work, the scattering intensity I(q) is equal to the sum of the coherent scattering that arises from the spatial correlation between identical components  $I_{ii}$  and the scattering due to the spatial relationship between two different components  $I_{ii}$ .<sup>7,8,17</sup>

$$I(q) = (\rho_i - \rho_s)^2 I_{ii}(q) + (\rho_j - \rho_s)^2 I_{jj}(q) + 2(\rho_i - \rho_s)(\rho_j - \rho_s) I_{ij}(q)$$
(3.2)

where i and j are the different components, s is the solvent, and  $\rho$  is the scattering length density (SLD). The scattering intensity from the individual components depends on the difference between the SLD of the material and the solvent.

#### **3.5.1 Contrast Matching**

In small angle scattering, a capability called contrast matching is leveraged to isolate scattering from a single component. This is achieved by varying the SLD of the material relative to the SLD of the solvent.

$$(\rho_{i} - \rho_{s}) >> (\rho_{j} - \rho_{s}) \text{ or } \rho_{j} = \rho_{s} \rightarrow I(q) \approx I_{i}(q) = (\rho_{i} - \rho_{s})^{2} I_{ii}$$
 (3.3)

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In neutron scattering, the SLD is defined as:<sup>18</sup>

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$$\rho_{\rm m} = \frac{\sum_{i=1}^{n} b_{\rm c,i}}{V_{\rm m}} \tag{3.4}$$

where  $b_c$  is the sum of the coherent scattering lengths for all the atoms in the material and  $V_m$  is the molecular volume of the material. The value of  $b_c$  varies between atomic isotopes. In this work, the contrasting  $b_c$  values for hydrogen (H) and deuterium (D) are used to match the SLD of the solvent to the SLD of the particles. The resulting scattering is dominated by the polymer. The same approach can be used to match the SLD of the solvent to the polymer to isolate scattering from the particles. The isotope concentration at which the solvent "matches" the scatterer is defined as the point of minimum scattering intensity (PMI). Table 3.2 lists experimental match points of various materials in water, and Figure 3.2 shows an illustration that summarizes contrast matching.

Material	PMI (mol%D <sub>2</sub> O)			
F127	12.2			
P123	13.4			
P103	12.7			
BSA	40.7			
Lysozyme	40.7			
Ferritin	52.0			

Table 3.2: Match points of various materials used in neutron scattering.<sup>2,14</sup>



Figure 3.2: Illustration of contrast matching.

For discrete scatterers, scattering intensity from a single material can be further deconstructed to

$$I_{ii}(q) = N(\rho_i - \rho_s)^2 V^2 S(q) P(q)$$
(3.5)

where N is the number density, V is the scatterer volume, P(q) is the form factor, and S(q) is the structure factor. The P(q) is experimentally measured by scattering from a dilute sample where there are negligible interactions between scatterers, and it provides information about the size and shape of the scatterer. The S(q)provides information on the spatial correlation between scatterers.

In x-ray scattering, the SLD is dependent on the atomic number of the different atoms in the material and is defined as:<sup>18</sup>

$$\rho_{\rm m} = \frac{\sum_{i=1}^{n} z_i r_e}{V_{\rm m}}$$
(3.6)

where z is the atomic number, and  $r_e$  is the radius of an electron. Rather than matching the SLD of the solvent to the material, contrast matching is achieved by adjusting the contrast in SLD between the material and solvent. Table 3.3 lists the SLD for these different materials that are used in this work.

Material	$\rho_m$ (Å <sup>-2</sup> )
Water (H <sub>2</sub> O)	9.4x10 <sup>-6</sup>
Pluronic <sup>®</sup>	9.7x10 <sup>-6</sup>
Gold	$1.3 \times 10^{-4}$
Silica	$1.9 \times 10^{-5}$

Table 3.3: SAXS scattering length densities for various materials.

#### 3.5.2 Rheo-SANS

Rheo-SANS experiments are performed at the NIST Center for Neutron Research (NCNR) in Gaithersburg, MD. Data is collected using either the NG7 30m, NGB 30m, or NGB 10m SANS instruments. For NG7 30m SANS, a neutron beam with wavelength of 6Å and spread of  $\Delta\lambda\lambda$  of 0.15 is used to collect scattering at sample-to-detector distances of 1.0m and 3.5m and cover a q range of 0.012<q<0.26Å<sup>-1</sup>. This instrument is used to gather structural data for 34wt% P103 (neat). For NGB 30m SANS, a neutron beam with wavelength of 6Å and a  $\Delta\lambda\lambda$  of 0.125 is used to collect scattering at sample-to-detector distances of 1.3m and 3.5m. At 1.3m, scattering is also collected with a detector offset of 25cm to increase the q range to 0.012<q<0.35Å<sup>-1</sup>. NGB 30m SANS is used to examine the structure of the P123 systems and the P103 systems with added protein. For NGB 10m SANS, a neutron beam with a wavelength of 5Å and a spread of  $\Delta\lambda\lambda$  of 0.132 is used to collect scattering at sample-to-detector distances of 4m and 1.2m to cover a q range of  $0.01 < q < 0.45 \text{Å}^{-1}$ . The 1-2 shear cell experiments are conducted on NGB 10m SANS.

Shear fields are applied to the soft solids by a Couette shear cell controlled by an Anton Paar Physica MCR 501 Rheometer (Anton Paar, Graz Austria). The Couette shear cell consists of a titanium cup and a titanium bob with a sample thickness of 1mm. The NG7 30m SANS experiments use a cup with I.D. = 50mm and a bob with O.D. = 48mm. The NGB 30m SANS experiments use a cup with I.D. = 29mm and bob with O.D. = 27mm. The samples are loaded as a liquid at  $5^{\circ}$ C and equilibrated for at least 5 minutes, and then heated to the desired temperature and equilibrated for at least 30 minutes prior to applying high amplitude oscillatory shear.

Figure 3.3 (a) shows the top view of the Couette shear cell. Two projections of the flow-aligned structure are collected by impinging the beam in the radial and tangential directions. The radial direction probes the 1-3 plane and the tangential direction probes the 2-3 plane (1 = velocity (v), 2 = gradient ( $\nabla$ ) 3 = neutral or vorticity (e)). Figures 3.3 (b) to (d) show how high amplitude oscillatory shear changes the radial scattering pattern and polycrystallinity of the system.<sup>15</sup> Prior to shear, the system is comprised of many micellar crystals, or a polycrystal, that produce a powder diffraction pattern made of isotropic rings. By applying high amplitude oscillatory shear, the micellar crystals align into a near "single crystal" that produces a Bragg diffraction pattern (b). The symmetry of the scattering pattern usually persists after the cessation of shear (c).



Figure 3.3: Schematic of the top view of the Couette shear cell used (a). Example of two-dimensional radial scattering patterns for a cubic system before, during, and after the application of shear (b, c, d).

A third projection of the crystal structure is gathered using a 1-2 Shear cell with the beam oriented in the vorticity direction. Figure 3.4 (a) shows the front view of the 1-2 shear cell. Scattering at various positions in the gap provides information about the homogeneity of the shear alignment and relative orientation of the crystal structure. For this study, the shear aligned structure is examined near the moving wall, in the center of the gap, and near the stationary outer wall. These locations correspond to approximately 0.2 mm, 0.5 mm, and 0.8 mm from the moving wall. All of the data is reduced using standard reduction protocols developed by NIST.<sup>20</sup>



Figure 3.4: Schematic of the 1-2 Shear Cell used (a). Scattering is collected near the moving wall, gap center, and outer stationary wall. These positions correspond to 0.2 mm, 0.5mm, and 0.8 mm from the moving wall.

### 3.5.3 Small angle x-ray scattering (SAXS)

Small angle x-ray scattering (SAXS) is performed using a Rigaku S-MAX3000 (The Woodlands, TX). Scattering is collected using a Cu K<sub> $\alpha$ </sub> source with a wavelength of 1.54Å at a sample-to-detector distance of 3.0m. Temperature is controlled using a Linkam LTS 350 control stage. The scattering vector (q) is calibrated using a silver behenate standard. Samples are loaded as a liquid into Glass Number 50 Capillaries (Hampton Research; Aliso Viejo, CA) that have an outer diameter of 1.0mm and wall thickness of 0.01mm. Scattering intensity as a function of q is obtained by radially averaging the two-dimensional scattering pattern.

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Chapter 4 Impact of dispersed particles on the structure and shear alignment of block copolymer soft solids

## 4.1 Introduction

The flow mechanism and structural parameters of these nanostructured soft materials are influenced by processing conditions, such as thermal history and applied flow fields. The structural parameters of these ordered materials cover lengthscales from nanometer through micrometer and larger, and respond to processing conditions differently. Structural parameters include the morphology of the micelle (i.e. spherical, cylindrical, lamella) $^{1-8}$ , the nature of the unit cell of the close packed micelle structure (i.e. FCC, BCC, HEX)<sup>3,4,6,7,9-14</sup>, and the polycrystallinity or defect structure of the soft solid.<sup>3,9,11,15–18</sup> At the nanometer and tens of nanometer lengthscales, operating temperature and thermal history influence both the micelle morphology and unit cell structure.<sup>3,6,7,10,12,19</sup> At the micron lengthscale, application of a flow field macroscopically aligns the micellar crystals into a single crystal, which corresponds to a decrease in polycrystallinity.<sup>11,16,20–22</sup> The mode of the flow, oscillatory versus steady shear, will alter the local packing and flow behavior of the micelles.<sup>16,21–24</sup> The applied flow field can change the close packed micelle structure from FCC to randomly close packed (RCP) spherical micelles<sup>21,25</sup>, destroy the ordered structure<sup>15,21,26</sup>, or shift the phase boundary (in a block copolymer melt).<sup>27</sup> These issues have been studied in block copolymer melts and solutions.

Here, we tackle the even more poorly understood problem of how the addition of nanoparticles dispersed in the solvent, affects these structural parameters and the flow mechanism.<sup>28</sup> Depending on the properties of the particles, the particles will reside at the interface between two polymer domains, in the defects such as grain boundaries, or in a specific polymer domain.<sup>17,29–31</sup> The added nanoparticles can change the close packed micelle structure from BCC to FCC<sup>32</sup>, HEX to LAM<sup>29</sup>, HEX to square packed cylindrical micelles (SQR)<sup>33</sup>, or disrupt the ordered micelle structure.<sup>34</sup> However, little information is known about how the added nanoparticles affect the flow mechanism of the soft solid.<sup>33,35</sup> Effective processing of these materials requires a detailed understanding of how processing affects the flow mechanism and structural parameters.

The particular block copolymer soft solids of interest are made from concentrated solutions of Pluronic<sup>®</sup> P123 and Pluronic<sup>®</sup> P103. Varying the block copolymer changes the properties of the micelles that form and the mechanics and structure of the resulting soft solids. As temperature increases, the structure of the polymer system changes from a disordered liquid to a cubic phase to a cylindrical phase.<sup>7,36</sup> The objective of this work is to demonstrate the effect of processing conditions and formulation on the cubic and cylindrical phases of soft solid. The formulation of the system is varied by adding globular proteins (bovine serum albumin (BSA) and lysozyme) to the interstitial spaces of the micellar structure how the added nanoparticles affect the flow mechanism of the soft solid.<sup>33,35</sup> The particle loading is roughly one protein for every two octahedral interstitial spaces. These systems are deformed using high amplitude oscillatory shear. Rheology measures the effect of added proteins and applied flow fields on the mechanical behavior of the system while small angle neutron scattering (SANS) with contrast

variation is used to gather crystallographic information about the soft solid. Using rheology and SANS, we demonstrate that proteins affect the shear alignment and structure of the soft solid. In the P123 system, the added BSA changes the flow behavior and relative stacking of close packed micellar planes in the cubic phase. Additionally, the added BSA changes the local structure of the cylindrical phase from hexagonally close packed to square packed micelles. In the P103 system, adding BSA decreases the shear alignment and changes the relative orientation of the micelles in both cubic and cylindrical phases. However, adding lysozyme to the P103 system does not appear to affect the mechanical behavior, shear alignment, or unit cell structure.

#### 4.2 Materials and Methods

The samples are prepared following the procedure in Section 3.3. For the Rheo-SANS experiments, samples with and without particles (neat) are prepared with protein-matched conditions so that all of the scattering data has the same incoherent scattering background and so the differences in density between the two solvents does not cloud the comparison.

For the rheometric experiments, samples are loaded according to the protocol in Section 3.4. Rheological temperature sweeps are used to measure the mechanical response of the system as the system is heated from 5°C to 45°C at a rate of 1°C/min. Modulus relaxation experiments are conducted for each of the ordered phases (cubic and cylindrical) using a Couette cell. After loading the samples as a liquid, they equilibrate at the desired temperature for 50 minutes prior to the application of high amplitude oscillatory preshear. The P123 systems

are studied at 17°C and 45°C while the P103 systems are studied at 25°C and 45°C. The P103 system with added BSA uses a preshear of 5Hz and 2500% for 3 minutes at 25°C and 5Hz and 500% for 5 minutes at 45°C. For the remaining P103 and P123 systems, a preshear of 5Hz and 1000% for 3 minutes is applied at 17°C/25°C and 45°C. After the applied preshear, the magnitude of the modulus is measured as a function of time at a fixed strain and frequency of 0.5% and 1 rad/s.

Rheo-SANS experiments are used to gather information about the structural features of the soft solid. The instrumentation and experimental setup are described in Section 3.5.2. The samples are examined at 17°C and 45°C for the P123 systems and 25°C and 45°C for the P103 systems. Between temperatures, the system is cooled to 5°C for at least 30 minutes to remove thermal and shear history effects. The preshear conditions are the same as those used for the rheology experiments. The P123 samples use high amplitude oscillatory preshear (5Hz, 1000%) for 4 minutes at 17°C and 45°C. The P103 sample with and without lysozyme are aligned using a preshear (5Hz, 1000%) for 15 minutes and 4 minutes, respectively. The P103 sample with added BSA has a preshear of 5Hz and 2500% for 4 minutes at 25°C, and 5Hz and 500% for 8 minutes at 45°C applied.

# 4.3 Results

The details of the phase behavior and structure for the P123 and P103 systems (without proteins) have been presented in the literature and verified here using visual observations, birefringence and small angle neutron or x-ray scattering.<sup>7,36</sup> In the neat P123 system, a isotropic phase of spherical micelles

packed in a FCC structure and a birefringent HEX structure are identified.<sup>7</sup> The neat P103 forms a isotropic phase made of spherical micelles packed in a BCC structure and a birefringent HEX structure.<sup>36</sup>

Figure 4.1 shows the magnitude of the complex modulus,  $|G^*|$ , as a function of temperature for both the P123 and P103 systems during heating from a liquid to a soft solid. Figure 4.1 (a) demonstrates the thermal response of the modulus for 35wt% P123 in water both with and without 3wt% BSA. The vertical lines represent the phase transition boundaries for 35wt% P123 in water, or neat system, and are consistent with previously reported results.<sup>7</sup> For 35wt% P123 in water, sharp transitions in the modulus are observed. At temperatures between 8°C and 12°C the modulus increases by about five orders of magnitude to approximately 25kPa. The modulus continues to increase with temperature before reaching a maximum of approximately 50kPa at 19°C. At temperatures above 19°C, the modulus gradually decreases with temperature to a value of 16kPa at 45°C. The rapid increase in the modulus between 8°C and 12°C is due to an orderdisorder transition (ODT), or a transition from a disordered viscous liquid to a soft solid.<sup>37–39</sup> The modulus of the liquid phase is low (a viscous liquid of  $\eta^* \sim 0.1$ Pa s) while the soft solid has a modulus of several tens of kPa. The ODT temperature  $(T_{ODT})$  is defined as temperature at the storage modulus (G') is greater than the loss modulus (G"). This is shown in Figure 4.1 (a) as the vertical dashed line at 12°C.

When observed between two crossed polarizing films, the system is not birefringent below 27°C but birefringent from 27°C to 45°C. Birefringence

indicates anisotropy of the structure on the length scale of the wavelength of light. Previous work on these block copolymer systems suggests that spherical micelles packed in a cubic structure will be isotropic while a lamellar or cylindrical phase will be birefringent.<sup>37,40</sup> The temperature at which birefringence is first seen is denoted as the order-order transition temperature ( $T_{OOT}$ ), or the temperature at which the system changes from one ordered phase to another. The  $T_{OOT}$  for the 35wt% P123 in water is 27°C and denoted by a dashed vertical line. The data for the P123 system with 3wt% BSA exhibits similar behavior to the neat P123 system (without particles). The  $T_{OOT}$  from 12°C to 16°C and decreases the magnitude of the complex modulus above 30°C. At 45°C, the system is still birefringent, but the added of BSA decreases the modulus by three decades from 16kPa to 0.02kPa.



Temperature (°C)

Figure 4.1: Magnitude of the complex modulus as a function of temperature for neat and composite systems containing 3wt% BSA or lysozyme. The samples are heated at a rate of 1°C/min and probed with small amplitude oscillations (0.5%, 1 rad/s). Results are for samples containing (a) 35wt% P123, and (b) 34wt% P103 (neat) and 35wt% P103 with proteins. The dotted lines denote temperatures at which the neat system undergoes an order-disorder transition (ODT) and order-order transition (OOT).

Figure 4.1 (b) shows the thermal behavior for both 34wt% P103 or 35wt%

P103 with added protein in water. The slight difference in polymer concentration

does not impact the results. The dashed vertical lines denote the  $T_{ODT}$  and  $T_{OOT}$ for the neat P103 system. The general behavior displayed by the neat P103 system is similar behavior to the neat P123 system. The modulus increases to approximately 25kPa between 12°C and 17°C indicating the system is going through an ODT ( $T_{ODT} = 17^{\circ}C$ ). The modulus continues to increase with temperature until reaching a plateau at approximately 40kPa above 18°C. Increasing the temperature from 29°C to 35°C decreases the modulus by an order of magnitude from 40kPa to 4.0kPa. Between 35°C and 45°C the modulus maintains this lower value of approximately 4.0kPa. Similar to the neat P123 system, birefringence experiments show the system goes through an OOT; the soft solid is isotropic below 27°C but birefringent between 27°C and 45°C. The  $T_{OOT}$  is indicated by the onset of birefringence at 27°C. Figure 4.1 (b) also shows the effect of two different types of globular proteins on the macroscopic behavior; lysozyme and BSA. From the rheological data, added lysozyme does not have a significant impact the modulus of the different ordered states or the on the macroscopic phase behavior. The addition of BSA has a more pronounced impact on the mechanical behavior. The addition of BSA increases the ODT from 17°C to 19°C and decreases the magnitude of the modulus above 24°C by several orders of magnitude. For this system, birefringence indicates the T<sub>OOT</sub> is between 25°C and 26°C, and the mechanical behavior is consistent with the optical change.

For this work, we focus on the impact of added proteins on both the cubic and cylindrical crystal structures. The temperatures used to characterize the cubic structures are 17°C for the P123 systems and 25°C for the P103 systems. The cylindrical structure is characterized at 45°C for both the P123 and P103 systems.

Figure 4.2 shows SANS data as radially averaged intensity as a function of  $q/q^*$  for the various samples at different temperatures, where  $q^*$  is the q position of the maximum intensity measured in the primary peak. The values of q\* are given in Table 4.1 and range from 0.03-0.05Å<sup>-1</sup> for these structures. The scattering profiles in Figure 4.2 are obtained by radially averaging the twodimensional powder scattering patterns. The same thermal history is used for all of the samples. Each is loaded as a liquid at 5°C, heated to the cubic temperature (17°C or 25°C) for measurements, cooled to 5°C for at least 30 minutes, and heated to the cylindrical temperature (45°C) for measurements. SANS is used to verify that cooling the samples to 5°C eliminated all structure at these lengthscales. The solvent is protein matched (40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O) to isolate scattering from the polymer phase in the polymer-protein composite systems.<sup>33</sup> Table 4.1 shows that the added protein does not significantly change the value of q\* for the P103 or P123 systems. Additionally, the P123 and P103 systems have comparable q\* values, which indicate the micelles that form are similar in size (diameter  $\sim 20$ nm).



Figure 4.2: Radially averaged I(q) from SANS powder scattering for samples containing P123 or P103 with and without dispersed proteins. The solvent (40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O) is matched to that of the proteins. Results are for samples containing (a) 35wt% P123 and (b) 34wt% P103 and 35wt% P103 with added proteins at 17°C or 25°C and 45°C. Symbols represent data for the neat systems (without proteins) (•), with BSA ( $\circ$ ), and with lysozyme ( $\Box$ ). The momentum vector q is normalized by the position of the primary peak (q\*). The values of q\* are given in Table 4.1. Symbols above the curves denote predicted peak positions for FCC ( $\nabla$ ), BCC ( $\nabla$ ), HEX (•), and SQR ( $\diamond$ ) structures.

Figures 4.2 (a) and (b) show scattering profiles for the 35wt% P123 at 17°C (cubic) and 45°C (cylindrical) and the 34wt% P103 at 25°C (cubic) and 45°C (cylindrical) as filled symbols. The symbols above the curves denote expected peak positions for FCC ( $\nabla$ ), BCC ( $\nabla$ ), HEX ( $\blacklozenge$ ), and square packed

cylinders (SQR) ( $\Diamond$ ) crystal structures based on the position of the primary peak being q\*. The q/q\* ratios for these structures are: FCC  $[1:\sqrt{4/3}:\sqrt{8/3}:\sqrt{11/3}:$  $\sqrt{12/3}$ :  $\sqrt{16/3}$ :  $\sqrt{19/3}$ ], BCC [1:  $\sqrt{2}$ :  $\sqrt{3}$ :  $\sqrt{4}$ :  $\sqrt{5}$ :  $\sqrt{6}$ :  $\sqrt{7}$ ], HEX [1:  $\sqrt{3}$ :  $\sqrt{4}$ :  $\sqrt{7}$ :  $\sqrt{9}$ ], and SQR [1:  $\sqrt{2}$ :  $\sqrt{4}$ :  $\sqrt{5}$ :  $\sqrt{8}$ ].<sup>40–42</sup> The reason for these choices will be clarified as the powder scattering does not provide the necessary peak resolution. For the neat P123 system, only the primary peaks at  $q/q^* = 1$  are distinguishable at 17°C and 45°C. Although the scattering profiles appear similar, Table 4.1 shows the value of q\* is temperature dependent. Increasing the temperature from 17°C to 45°C decreases q\* indicating a small increase in the spacing of the micelles as the morphology of the soft solid changes from cubic to cylindrical. The change in the local structure of the soft solid is supported by the fact that the value of q\* is temperature dependent. In Figure 4.2 (b), the scattering profile for the neat P103 system at  $25^{\circ}$ C has a distinct primary peak at  $q/q^* = 1$  as well as a shoulder at  $q/q^* = 1.4$  (~ $\sqrt{2}$ ). At 45°C, there is a primary peak as well as a low intensity peak at  $q/q^* = 2.9 (\sim \sqrt{9})$ .

	Т	Powder	At cessation of shear			At rest		
Sample	(°C)	q* (Å <sup>-1</sup> )	$q^{*}(Å^{-1})$	$q_2(Å^{-1})$	q <sub>3</sub> (Å <sup>-1</sup> )	q* (Å <sup>-1</sup> )	$q_2 (Å^{-1})$	q <sub>3</sub> (Å <sup>-1</sup> )
P123 neat	17	0.046	0.043	0.071	0.083	0.043	0.071	0.083
	45	0.038	0.038	0.061	0.100	0.038	0.063	0.100
P123+BSA	17	0.045	0.042	0.068	0.082	0.043	0.069	
	45	0.036	0.035	0.051	0.069	0.035	0.051	0.069
P103 neat	25	0.048	0.044	0.073	0.087	0.045*	0.070*	0.085*
	45	0.041	0.041	0.070		0.042*	0.070*	
P103+BSA	25	0.048	0.047			$0.047^{+}$		
	45	0.040	0.040			0.040		
P103+LYS	25	0.048	0.045	0.072	0.086	0.045	0.072	0.086
	45	0.042	0.042	0.070		0.042	0.070	

Table 4.1: Values of q from SANS for the primary peak (q\*) and higher order peaks. The value of q\* from the powder scattering is determined by radially averaging I(q) from radial powder scattering patterns and taking the q\* to be value with the maximum intensity. For scattering collected after the cessation of shear, q values are equivalent to the positions of the Bragg spots in the radial patterns. The error of the q\* values is approximately 0.003 Å<sup>-1</sup>. The higher order q values and those obtained from the 1m data have a slightly larger error; however it does not significantly affect the results of the analysis. (\*) and (<sup>+</sup>) indicate values are from scattering collected after 1hr and 6hrs, respectively.

The SANS intensity for the P123 and P103 systems with added protein (Figures 4.2 (a) and (b)) are shown as open circles. Note that the solvent is matched to the protein, so scattering is predominantly from the micelle structure. For the P123 system with added BSA (Figure 4.2 (a)), primary peaks at  $q/q^* = 1$  are distinguishable at both temperatures. Higher order peaks are not observed at 17°C, but there is a shoulder at  $q/q^* = 1.4$  ( $\sim \sqrt{2}$ ) at 45°C. The scattering profile for the P103 system with added BSA at 25°C (Figure 4.2 (b)) has a primary peak as well as a low intensity peak at  $q/q^* = 1.9$  ( $\sim \sqrt{4}$ ). At 45°C, there is a primary peak at  $q/q^* = 1$  but no higher order peaks are observed. The P103 system with the smaller protein lysozyme has peaks at  $q/q^* = 1$  and 1.9 ( $\sim \sqrt{4}$ ) at 25°C and at

 $q/q^* = 1$  and 2.6 (~ $\sqrt{7}$ ) at 45°C, which suggests the unit cell structure is the same as the neat system.

The crystal structure cannot be identified solely from the scattering of a polycrystalline system (Figure 4.2), due to the low peak resolution from wavelength smearing and loss of higher order peaks from minima in the micelle form factor.<sup>43</sup> Therefore, the expected structures are based on previously reported results. A soft solid made from 35wt% P123 has FCC structure at 17°C and a HEX structure at 45°C.<sup>7</sup> A soft solid made from 34wt% P103 has BCC structure at 25°C and a HEX structure at 45°C.<sup>36</sup>

Shear is shown to be effective in macroscopically aligning the micellar crystals into a near "single crystal."<sup>20,31</sup> Here, we apply a large amplitude oscillation to align and anneal the structure without tearing the soft solid or inducing shear banding.<sup>35</sup> We refer to this high amplitude oscillation as a "preshear". Figure 4.3 shows the relaxation of the complex modulus after the cessation of a high amplitude oscillatory preshear for both the neat and composite systems. At time zero, the high amplitude preshear is stopped. The complex modulus is measured for 90 minutes after the cessation of preshear using a small amplitude oscillation (0.5% and 1 rad/s), low enough to be considered a probe of the structure. The magnitude of the modulus prior to shear (while the system is a powder) is included for comparison and represented by the symbols on the left axis.

For the two neat systems in the cubic phase (Figures 4.3 (a) and (c)), the modulus is essentially insensitive to shear alignment and time after the cessation

of shear. There is a small drop in the value of the modulus after the preshear is applied with limited recovery over time. This suggests that the modulus of the powder and aligned crystal are similar and do not change after shear. For the two neat systems in the cylindrical phase (Figures 4.3 (b) and (d)), the mechanical properties are impacted by preshear. For the P123 system, the modulus drops by more than an order of magnitude from the powder to aligned state; this suggests that the polycrystal is a quasi-stable state that is easily aligned. For P103 a similar behavior is observed but the drop is not as significant. The modulus of the aligned cylindrical state of the P103 system is higher than the P123 system even though this is reversed in the polycrystalline state (Figure 4.1).



Figure 4.3: Magnitude of the complex modulus  $|G^*|$  as a function of time for neat and composite systems after cessation of shear. Results are for samples containing (a)-(b) 35wt% P123 and (c)-(d) 34wt% P103 (neat) and 35wt% P103 (composite) with 3wt% BSA or lysozyme. The symbols on the left axis correspond to the value of  $|G^*|$  measured before shear for neat systems (•), with lysozyme (□), and with BSA ( $\circ$ ). The vertical dashed lines and right axis denote the times at which SANS data is collected (5 min and 90 min after cessation of flow).

The addition of BSA has limited impact on the properties of the P123 cubic phase, but does alter the flow behavior of the P103 cubic phase; in this case

shear alignment causes the modulus to drop by nearly two orders of magnitude and then recover slowly (over~30 minutes) to a value about an order of magnitude lower than the powder. The addition of BSA does impact the cylindrical phase of both systems, as the moduli are lower in the powder and aligned states. For the P123 cylindrical phase with BSA, the modulus of the aligned state recovers over time but only partially. For comparison another protein with smaller size, lysozyme, was also added to the two systems, but the mechanical behavior is not altered.

To connect these mechanical measurements to structure, we measure the structure of the micellar phase immediately after the cessation of shear and after a relaxation on timescales similar to those in Figure 4.3. The vertical dotted lines in Figure 4.3 represent points at which structural measurements are performed. SANS data is collected for 5 minutes and is taken 5 minutes after the cessation of shear ("cessation of shear") and after 90 minutes at rest ("rest"). Based on the results in Figure 4.3, we expect the preshear to align the micellar crystals into a persistent "single crystal." The exceptions to this are the P123 cylindrical phase and P103 cubic phase which are expected to display transient structural behavior on same the timescales as the rheological data.

Figure 4.4 shows two-dimensional scattering patterns for the cubic and cylindrical phases of the P123 systems that have been aligned by preshear. Both radial and tangential patterns are shown at 5 minutes after the cessation of the preshear. A radial pattern is also shown at 90 minutes after the cessation of shear. Scattering intensity collected at a sample-detector distance of 3.5m is shown for

convenience. Data is also collected at 1.0m to provide higher order peaks but is not included in Figure 4.4. The intensity of the tangential patterns is greater on one side of the pattern due to the curvature of the cell. Table 4.1 shows the values of q for the primary and higher order rings in the radial scattering patterns.

Figure 4.4 (a) shows scattering collected for the P123 systems in the cubic phase. Radial scattering for the neat P123 system after the cessation of shear has six equidistant Bragg spots in both the primary and secondary rings. The 1.0m data not presented shows the third ring also has Bragg spots with six-fold symmetry. The radial pattern collected at rest has the same symmetry and spot positions indicating the shear alignment is persistent. From the peak positions given in Table 4.1, the relative positions of these rings are at approximately  $q/q^* = 1, \sqrt{8/3}$ , and  $\sqrt{11/3}$ . For the tangential pattern, the inner ring  $(q^* = 0.045 \text{ Å}^{-1})$  has two Bragg spots on the equator with smeared off-axis spots. The distinct Bragg spots indicate the micelles have formed a well-defined crystal.

The patterns for the P123 system with BSA (Figure 4.4 (a)) shows scattering from the polymer micelles in the polymer-particle composite system. In the cubic phase after the cessation of shear, the inner and outer rings in the radial pattern each have Bragg spots with six-fold symmetry. The relative position of these rings are at values of  $q/q^* = 1, \sqrt{8/3}$ , and  $\sqrt{11/3}$ , and tabulated in Table 4.1. At rest, the six spots previously displayed in the primary ring appear to have split into multiple spots. The second order ring is still visible with six equally spaced spots, but the third order ring is no longer discernable. In the tangential scattering, the primary ring at  $q^* = 0.044$ Å<sup>-1</sup> has two spots on the equator as well

as four spots at  $\pm 70^{\circ}$  from the horizontal. The second order ring at  $q = 0.050 \text{Å}^{-1}$  has four spots at  $\pm 55^{\circ}$ , and the third order ring at  $q = 0.071 \text{Å}^{-1}$  has four low-intensity spots at  $\pm 35^{\circ}$  from the horizontal. The relative positions of these rings are at  $q/q^* = 1$ ,  $\sqrt{4/3}$ , and  $\sqrt{8/3}$ .



Figure 4.4: Two-dimensional scattering patterns for the 35wt% P123 with and without 3wt% BSA after the cessation of shear (5Hz, 1000%). The scattering length density of the solvent (40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O) is matched to the protein. Scattering patterns are for the (a) cubic phase at  $17^{\circ}$ C and (b) cylindrical phase at  $45^{\circ}$ C after the cessation of shear.

To clearly show the change in the radial scattering for the P123 system with BSA, Figure 4.5 shows a plot of scattering intensity as a function of azimuthal angle at a value of  $q^*$  for patterns in Figure 4.4 (a). The azimuthal angle is the angle relative to the velocity direction. At 5 minutes, there are six distinct peaks located at  $30^\circ$ ,  $90^\circ$ ,  $150^\circ$ ,  $210^\circ$ ,  $270^\circ$ , and  $330^\circ$ . At 90 minutes, the previous six high-intensity peaks have turned into six low-intensity peaks. There are also additional peaks located at  $0^\circ$  and  $180^\circ$ , and the peaks at  $90^\circ$  and  $270^\circ$  have low amplitude peaks located directly to the left and right of them. Since the features of the scattering intensity change over time, the shear aligned state is not maintained.



Azimuthal Angle,  $\phi$  (degree)

Figure 4.5: Scattering intensity versus azimuthal angle for the primary ring of the radial scattering patterns for the patterns in Figure 4.4. Scattering is for 35wt% P123 with 3wt% BSA at  $17^{\circ}$ C at the cessation of shear (•) and at rest ( $\circ$ ). Data is shifted vertically for clarity.

In both systems, the powder is aligned into a near single crystal by the oscillatory shear. For the neat P123 system in the cubic phase (Figure 4.4 (a)), the radial and tangential patterns are consistent with scattering simulated for a random close packed (RCP) structure with the close-packed (111) plane oriented parallel to the velocity direction.<sup>7,11,25,26,35</sup> An RCP structure is comprised of randomly stacked hexagonally close packed layers of micelles and can also be described as a mix of FCC and hexagonally close packed (HCP) structures. For the composite P123 system in the cubic phase, the six-fold pattern seen in the radial pattern is consistent with scattering predicted for a RCP structure with the (111) planes parallel to the velocity direction. However, the tangential pattern, which provides information relevant to the stacking of the close packed layers of micelles, corresponds to scattering predicted for a twinned FCC crystal structure.<sup>11,21,35</sup> Therefore, the addition of protein to the cubic crystal does not interfere with the hexagonally close packed layers, but does stacking of the layers changes from an RCP to a predominately twinned FCC stacking. In the composite system, the transition in the scattering intensity is a due to the stacking of layers to slowly changing with time, which suggests that the protein is disrupting the layer stacking. This is consistent with the mechanical behavior shown in Fig 4.3 (a). The modulus of the composite slightly increases after the cessation of shear, consistent with the decorrelation of the stacked layers.

Comparison of the primary peak positions, in Table 4.1, for the neat and composite P123 systems before and after preshear shows that value of q\* is lower

after the cessation of shear. This decrease in q\* has been observed in other shearaligned block copolymer systems with RCP/HCP/FCC structures.<sup>21,24</sup>

Figure 4.4 (b) shows the same set of two-dimensional patterns for the P123 system with and without BSA in the cylindrical phase at 45°C. For the neat P123 system, the radial pattern collected after the cessation of shear has two meridional spots as well as four low-intensity off-axis spots in the primary ring. Figure 4.6 shows the intensity as a function of azimuthal angle for the scattering collected immediately after shear. The two high-intensity peaks at  $90^{\circ}$  and  $270^{\circ}$ correspond to the two meridonal peaks seen in the radial scattering pattern. The four low-amplitude peaks located at  $\pm 35^{\circ}$  correspond to the off-axis peaks displayed in two-dimensional pattern. There are also two meridional spots located in the higher order ring. Radial scattering collected after relaxation continues to have the same distinct meridional spots in the primary and higher order rings, but the off-axis spots in the inner ring have decreased in intensity. The primary ring of the tangential pattern at  $q^* = 0.038 \text{\AA}^{-1}$  has six equidistant spots (with two of the spots along the equator) in addition to two meridional spots and several other low intensity spots located at  $a \pm 30^{\circ}$  from horizontal.



Figure 4.6: Scattering intensity versus azimuthal angle for the primary ring of the radial scattering for 35wt% P123 at 45°C collected immediately after shear (Figure 4.4 (b)).

For the composite P123 system, radial scattering after the cessation of shear has two meridional spots in the primary and higher order rings. Compared to the neat P123 system, adding BSA results in the disappearance of the off-axis spots and decreases the position of q\*. The symmetry and q\* position of radial patterns remains unchanged after 90 minutes indicating a persistently aligned state, even though the mechanical behavior shows a transient (Figure 4.3 (b)). In the tangential pattern, the primary and secondary rings have four spots in a square configuration, and the third ring has two visible meridional spots. The q positions of these rings are 0.035, 0.048, and 0.069Å<sup>-1</sup>, comparable to the data given in Table 4.1.

In Figure 4.4 (b), radial scattering provides information regarding the orientation of the cylindrical micelles relative to the shear direction, and the

tangential scattering information about the local packing of the micelles. Table 4.1 shows that the value of q\* for the cylindrical phase does not change after the preshear. For the neat P123 system immediately after shear, the two meridional spots in the radial pattern indicate the cylindrical micelles are oriented parallel to the velocity direction.<sup>6,44</sup> The off-axis spots have been attributed to bends or undulations in the cylindrical micelles.<sup>45</sup> From the tangential scattering, the sixfold pattern in the inner ring is indicative of hexagonally close packed cylindrical micelles, and the additional meridional spots and other low-intensity spots are likely attributed to the undulations in the micelles. For the composite P123 system, the two meridional spots in the radial pattern indicate the cylindrical micelles are oriented parallel to the velocity direction, as in the neat system. In the scattering tangential pattern, the square symmetry along with the  $q/q^*$  positions  $(q/q^* = 1:\sqrt{2}:\sqrt{4})$  correspond to cylindrical micelles packing in a square conformation.<sup>46</sup> The added BSA induces a structural change from a HEX to a SQR structure. This particular structural change has also been observed in 33wt% P123 with 3wt% BSA at 40°C (cylindrical phase) but had to be identified using only the radial scattering patterns collected for a system under steady shear.<sup>33</sup> The SQR structure has also been produced in block copolymer thin films through chemical and topological templating, confinement, and directed assembly but not spontaneously formed in the bulk as seen here.<sup>46</sup>

Figure 4.7 shows two-dimensional scattering patterns for the P103 systems in the cubic and cylindrical phases after the cessation of shear, in the same layout as Figure 4.4. Table 4.1 shows the value of q for the primary and higher order rings for the radial scattering patterns. Figure 4.7 (a) shows the scattering patterns for the P103 systems in the cubic phase. The radial scattering for the neat P103 system has three rings with six-fold symmetry. The relative position of the rings are at q/q\* values of approximately  $1, \sqrt{3}$ , and  $\sqrt{4}$ . The symmetry and position of the Bragg spots remain unchanged at rest indicating the alignment is persistent, consistent with the constant modulus in Figure 4.3 (c). The tangential scattering pattern has six equidistant spots along with two meridional spots in the primary ring q\* = 0.048Å<sup>-1</sup>. For the P103 system with added BSA, the radial scattering collected after the cessation of shear has six spots with hexagonal symmetry in the primary ring. This same pattern is observed after 6 hours at rest indicating the aligned state persists. The tangential scattering pattern has an isotropic primary ring at q\* = 0.048Å<sup>-1</sup>.

The radial scattering for the neat P103 system in the cubic phase (Figure 4.7 (a)) is consistent with scattering from the (111) plane of a BCC crystal structure.<sup>47,48</sup> However, the tangential pattern is the result of scattering from multiple planes of a BCC crystal rather than from a single plane. This tangential pattern is consistent with scattering from the (111) and (112) planes of a BCC crystal. For the P103 system with BSA, the radial scattering lacks higher order rings and tangential scattering lacks Bragg spots that are typically exhibited for a well aligned system. The lack of these features indicates the BSA reduces the overall alignment of the cubic phase. Additionally, the absence of these key scattering features makes it difficult to gather crystallographic information about

the soft solid, but the hexagonal ring in the radial pattern does indicate the spherical micelles form a cubic structure.



Figure 4.7: Two-dimensional scattering patterns for the 34wt% P103 and 35wt% P103 with 3wt% BSA after the cessation of shear. The scattering length density of the solvent (40.7mol  $D_2O\%$ :59.3mol%  $H_2O$ ) is matched to the protein. Scattering patterns are for the (a) cubic phase at 25°C and (b) cylindrical phase at 45°C. Radial and tangential scattering patterns are collected 5min and 90min after the cessation of shear unless otherwise noted.

Figure 4.7 (b) shows the two-dimensional patterns for the P103 systems in

the cylindrical phase at 45°C. For the neat and composite P103 systems, Table 4.1

shows the value of  $q^*$  for the cylindrical phase is the same before and after the application of shear. For the neat P103 system, radial scattering patterns collected at the cessation of shear and at rest have two meridional spots in the primary ring. The radial pattern remains unchanged indicating that the alignment of the cylindrical micelles is persistent. The tangential pattern has six equidistant spots in the primary ring at  $q^* = 0.041$ Å<sup>-1</sup>. Scattering for the neat system in the cylindrical phase is similar to scattering of the neat P123 system (Figure 4.4 (b)). However, the increased breadth of the Bragg spots indicate the P103 cylindrical phase is not as well aligned. The position and symmetry of the Bragg spots indicates the cylindrical micelles align parallel to the velocity direction and organize into a HEX structure.<sup>6,44,49</sup>

Dispersing BSA into the soft solid changes the symmetry of the radial and tangential scattering patterns. Unlike the neat P103 system, the tangential scattering pattern has two equatorial spots in the primary ring ( $q^* = 0.041 \text{ Å}^{-1}$ ). The radial pattern changes from having two broad meridional spots after the cessation of shear to two equatorial spots at rest. Figure 4.8 shows a plot of intensity as function of azimuthal angle to clearly show how the azimuthal dependence changes with time. On the left is the scattered intensity as a function of azimuthal angle and the corresponding two-dimensional patterns are shown on the right. While the system is under shear (Figure 4.8 (a)), the primary ring has two peaks at 90° and 270°. These peaks correspond to the two meridonal spots in the two-dimensional pattern. Five minutes after the cessation of shear (Figure 4.8 (b)) the scattering intensity has two broad peaks that appear as smeared meridonal
spots in the two-dimensional pattern. At 90 minutes after the cessation of shear (Figure 4.8 (c)), the scattering intensity has two peaks at  $0^{\circ}$  and  $180^{\circ}$ , which match the equatorial spots in the two-dimensional pattern.



Figure 4.8: Scattering intensity versus azimuthal angle for the primary ring of the radial scattering patterns for 35wt% P103 with 3wt% BSA at 45°C during and after shear (500% and 5Hz). (a) Data collected during shear ( $q^* = 0.040 \text{\AA}^{-1}$ ); (b) data collected 5 min after the cessation of shear ( $q^* = 0.040 \text{\AA}^{-1}$ ); (c) data collected 90 min after the cessation of shear ( $q^* = 0.040 \text{\AA}^{-1}$ ). The corresponding two-dimensional scattering patterns are shown on the right.

The time dependence of the scattering intensity shows that the BSA affects the flow mechanism and the relative orientation of the micelles. The equatorial spots seen in the tangential pattern and radial pattern at rest are consistent with cylindrical micelles oriented parallel to the vorticity direction. Interestingly, the two equatorial spots in the radial pattern are also seen prior to shear (Appendix A), suggesting the added BSA preferentially and persistently aligns the cylindrical micelles parallel to the vorticity direction. These results

further imply that the added shear is not able to change the alignment of this persistently aligned state.

Relative to the neat P103 system, the addition of BSA increase the breadth of the Bragg spots indicating the BSA reduces the alignment of the cylindrical phase. Since the tangential pattern does not show the six equidistant spots, it cannot be confirmed that the cylindrical micelles arrange in a HEX structure. In Figure 4.3 (d), the mechanical relaxation shows that the addition of particles decreases modulus by several orders of magnitude before and after preshear, suggesting the added BSA disrupts the cylindrical phase; however, the relaxation does not capture the transient structural behavior that occurs after the cessation of shear.

Figure 4.9 shows measured scattering patterns for the neat P103 system in the cubic phase and corresponding predicted diffraction patterns. Figures 4.9 (a), (b), and (c) compare scattering in the radial, tangential, and 1-2 directions, respectively. The radial pattern (Figure 4.9 (a)) is consistent with scattering from the (111) plane of a BCC crystal that is predicted to have rings comprised of six equidistant Bragg spots at  $q/q^* = 1, \sqrt{3}$ , and  $\sqrt{4}$ .<sup>48</sup>



Figure 4.9: Proposed diffraction patterns for the neat P103 system in the cubic phase. The two-dimensional scattering patterns for 34wt% P103 at  $25^{\circ}\text{C}$  are shown on the top while the corresponding diffraction patterns for a twinned BCC crystal are shown below. (a) Diffraction pattern collected with the beam scattering from the (111) plane. (b) Diffraction pattern collected with the beam scattering from the (111) and (112) planes. (c) Diffraction pattern collected with the beam scattering from the (110) and (112) planes. (•) are Bragg spots due to scattering from the (111) plane, (•) are Bragg spots due to scattering from the (111) plane, (•) are Bragg spots due to scattering from the (111) plane, (•) are Bragg spots due to scattering from the (111) plane, (•) are Bragg spots due to scattering length density of the solvent is protein-matched (40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O) for the radial and tangential scattering, and 100% D<sub>2</sub>O for the 1-2 scattering.

The tangential pattern in Figure 4.9 (b) is consistent with scattering predicted from the (112) and (111) planes of a BCC crystal. The two meridional spots are scattering from the (112) plane while the six hexagonal spots are scattering from the (111) plane. Scattering in the 1-2 direction (Figure 4.9 (c)) has two strong equatorial spots and four spots at  $\pm$  55° from the velocity direction in the primary ring at q\* = 0.046Å<sup>-1</sup>. This is consistent with scattering predicted from multiple planes of a twinned BCC crystal. The equatorial spots are due to

scattering from the (112) plane while the off axis spots are due to scattering from the (110) plane.<sup>50</sup> The three projections of the crystal structure suggest the P103 cubic phase aligns into a twinned BCC crystal with the (111) plane parallel to the shear direction.

The radial pattern in Figure 4.9 (a) has been reported for Pluronic<sup>®</sup> F88 (which has a BCC structure). The radial scattering pattern is due to scattering from the (111) plane of a BCC crystal while the tangential scattering (which is not shown) is due scattering from the (112) plane.<sup>20</sup> A rotation of this orientation is reported for a poly(ethylenepropylene)-poly(ethylethylene) diblock copolymer melt with BCC structure.<sup>50</sup> Additionally, this tangential pattern has been reported for a solution of poly(styrene-isoprene) in diethyl phthalate that has a mixture of BCC and hexagonal close packed structures.<sup>6</sup>

To resolve the rapid transient seen in the mechanical behavior in Figure 4.3 (c) for the BSA loaded cubic phase of P103, Figure 4.10 shows twodimensional radial patterns for the P103 system with BSA at 25°C during shear and immediately after the cessation of shear, in one minute increments. This system is expected to be a cubic phase at rest. During shear, the scattering pattern has two meridional spots in the primary ring (q\* =  $0.046 \text{Å}^{-1}$ ). Scattering intensity collected in the first two minutes after the cessation of shear also have two meridional spots in the primary ring q\* =  $0.049 \text{Å}^{-1}$ . At three minutes after the cessation of shear, the scattering pattern has a six-fold symmetry and the q\* shifts from  $0.049 \text{Å}^{-1}$  to  $0.048 \text{Å}^{-1}$ . The six-fold pattern persists for at least six hours (Figure 4.7 (a)). The addition of BSA does shift the OOT (Figure 4.1) so this is likely a shear-induced transition to a HEX phase that recovers over minutes to a cubic phase. Changes in the scattering pattern occur on the timescale of minutes and coincide with the transient mechanical behavior.



Figure 4.10: Two-dimensional radial scattering patterns for 35wt% P103 with 3wt% BSA collected during and directly after the cessation of shear. Scattering patterns after shear are presented in 1 minute increments for the first 5 minutes. The scattering length density of the solvent (40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O) is matched to the protein. This corresponds to the mechanical response seen in Figure 4.3 (c).

The rheological data in Figures 4.1 and 4.3 show that adding the smaller protein lysozyme does not impact the mechanical behavior of the P103 soft solid in the powder and shear aligned states. To determine the impact of lysozyme on the shear aligned structure, Figure 4.11 shows two dimensional scattering patterns for the P103 system with added lysozyme after the cessation of shear. In the cubic phase (Figure 4.11 (a)), radial scattering collected after the cessation of shear and at rest have clearly defined rings with six-fold symmetry. The primary ring also has four lower intensity spots located at approximately  $\pm 40^{\circ}$  from the horizontal that become more distinguishable with time. The tangential pattern is similar to that of the neat P103 system (Figure 4.7 (a)) with six equidistant spots along with two meridional spots in the primary ring q\* = 0.048Å<sup>-1</sup>.

Comparison of these scattering patterns to those of the neat P103 system (Figures 4.7 (a)) shows the added lysozyme does affect the shear alignment of the

cubic phase. Similar to the neat P103 system, the radial patterns have rings located at  $q/q^*$  values of 1,  $\sqrt{3}$ , and  $\sqrt{4}$  that are consistent with scattering from the (111) plane of a BCC crystal. Unlike the neat P103 system, radial scattering collected 5 and 90 minutes after the cessation of shear show the four low-intensity spots at a  $\pm 40^\circ$  become more distinct with time. This suggests that the orientation of the crystal is changing and the alignment is not as persistent. The four lower intensity spots could be due to scattering from the (100) plane of a BCC crystal, which is predicted to have four spots in the primary ring at  $\pm 45^{\circ}$ .<sup>47</sup> The tangential pattern is the same as for the neat P103 system (Figure 4.7 (a)), which is consistent with scattering from (112) and (111) planes of a BCC crystal. Furthermore, the q\* value of the aligned state is lower than the q\* of the powder and is consistent with the trend displayed by the neat system.



Figure 4.11: Two-dimensional scattering patterns for 35wt% P103 with 3wt% lysozyme after the cessation of shear. The scattering length density of the solvent (40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O) is matched to the protein. Scattering patterns are for the (a) cubic phase at  $25^{\circ}$ C and (b) cylindrical phase at  $45^{\circ}$ C.

Figure 4.11 (b) shows scattering for the P103 system with added lysozyme in the cylindrical phase. The radial scattering patterns have two meridional spots in the primary ring indicating the alignment persists, and the tangential pattern has six equidistant spots in the primary ring  $q^* = 0.042$ Å<sup>-1</sup>. The value of  $q^*$  (Table 4.1) is the same before and after the application of shear. The radial and tangential scattering patterns have the same symmetry as the scattering for the neat P103 system in the cylindrical phase, which shows the added lysozyme does not affect the shear alignment or flow mechanism of the cylindrical micelles.

Scattering in the 1-2 direction at several positions in the gap shows the shear alignment of the micelles is either homogeneous or nearly homogeneous throughout the gap. Figure 4.12 shows show two-dimensional 1-2 scattering patterns that demonstrate homogeneous and nearly homogenous shear alignment, respectively. Figure 4.12 (a) is show 1-2 scattering indicative of homogeneous alignment throughout the gap. This data is for 35wt% P123 with 3wt% BSA in a protein-matched solvent (40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O) at 45°C (cylindrical). The scattering patterns have two distinct equatorial spots and appear the same at each gap position indicating homogeneity of the shear alignment, crystal structure, and orientation of micelles through the gap. Figure 4.12 (b) shows 1-2 scattering indicative of nearly homogenous alignment. This data is for 34wt% P103 in 100% D<sub>2</sub>O at 25°C (cubic). The scattering patterns for the near the moving wall and center appear to be the same. They have two higher intensity equatorial spots and four lower intensity off-axis spots. Farther from the moving wall, or near the stationary outer wall, the scattering pattern changes; the position of the spots is still the same, but the clarity and anisotropy of the spots is different. The consistency of the spot positions indicates the orientation of the crystal structure relative to the shear direction is uniform throughout the gap. However, the change in the clarity and anisotropy of the spots indicates the degree of alignment decreases farther from the moving wall.



Figure 4.12: 1-2 scattering is collected near the moving wall, gap center, and outer stationary wall. These positions correspond to 0.2 mm, 0.5mm, and 0.8 mm from the moving wall. Two-dimensional scattering patterns are for (a) 35wt% P123 with 3wt% BSA (40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O) at  $45^{\circ}$ C and (b) 34wt% P103 in 100% D<sub>2</sub>O at  $25^{\circ}$ C. The scattering is from the polymer micelles in the system.

## 4.4 Discussion

The unit cell structure of the cubic phase is dependent on the block lengths of the triblock copolymer. The dimensions of the unit cell structure are estimated using the position of the primary peak along with the assumption of hard sphere interactions between the micelles and that the micelle core is fully dehydrated PPO. For the P123 cubic phase, the spherical micelles have a core diameter of 12nm and an overall diameter of 18nm. The spherical micelles form hexagonally close packed layers stacked in a repeated pattern to produce a FCC structure. Based on the geometry of the unit cell, the interstitial space is approximately 7nm. Application of shear de-correlates the close packed layers, resulting in random stacking of the micelle layers, or a RCP structure. In the P103 cubic phase, the spherical micelles organize into a BCC structure. The spherical micelles have a core diameter of 12.3nm and an overall diameter of 17.5nm, while the interstitial spacing is smaller at only 5nm.

Spherical micelles with thinner coronas, or "crew-cut" micelles, have been shown to preferentially organize into a FCC cubic structure, whereas thicker coronas, or "hairy" micelles, preferentially organize into a BCC cubic structure.<sup>4,10,19</sup> In this work, the P123 and P103 spherical micelles have relatively thin coronas of approximately the same dimensions. Based on these observations, the P123 and P103 spherical micelles are expected to form a FCC structure, yet the P103 system forms a BCC structure. A possible reason for the discrepancy between the observed and predicted structures is the presence of impurities (residual homopolymer and diblock copolymer) in the system formed during the synthesis. The impurities have been shown to affect the unit cell structure of Pluronic<sup>®</sup> F127, which is made of spherical micelles with relatively thick coronas. Using the Pluronic<sup>®</sup> F127 as received produces a FCC crystal structure; however, removal of the impurities results in a BCC crystal structure consistent with the predicted structure for a "hairy" micelle. Therefore, it is possible that the

impurities in the system are controlling the unit cell structure of the P103 soft solid.

Incorporating BSA ( $D_h \sim 7nm$ ) affects the shear alignment of the cubic phase for both P123 and P103 systems. In the P123 cubic phase, the added BSA changes the stacking of the micellar planes from a RCP to twinned FCC stacking. The added BSA keeps the micellar planes correlated during shear so that the repeated stacking pattern is maintained, however the alignment does not persist. In the P103 cubic phase, adding BSA results in transient mechanical and structural behavior that occurs on the timescale of minutes and makes it more difficult to alignment the micellar crystal.

The cylindrical phase in the P123 and P103 systems has the same HEX structure. The dimensions of the micelles are similar. The P123 cylindrical micelles have a core diameter of 10nm and an overall diameter of 19nm while the P103 cylindrical micelles have a core diameter of 9.2nm and an overall diameter of 17.7nm. The SANS data (Figures 4.4 (b) and 4.7 (b)) shows that the applied shear affects the P123 and P103 cylindrical phases differently. The primary differences being that radial scattering for P123 has off-axis spots and sharper spots compared to the P103 system. This suggests that P123 cylinders are more flexible able to undulate while the P103 cylindrical phases is sometimes attributed to a decrease in the persistence length of the micelle.<sup>45</sup> A study on uncrosslinked wormy micelles made from poly(ethylene oxide) based diblock copolymers showed the persistence length ( $l_p$ ) is proportional to the stiffness of the micelle

( $\kappa$ ), which in turn is proportional to the core diameter ( $d_{core}$ ) to the third power ( $l_p \sim \kappa \sim d_{core}^3$ ).<sup>51</sup> Assuming this relation holds for Pluronic<sup>®</sup> cylindrical micelles, the persistence length of P123 micelles is almost 30% greater than P103 micelles and would suggest P123 micelles are stiffer and less flexible.

Although the P123 and P103 cylindrical phases have the approximately the same structure and dimensions, the added BSA affects the two systems very differently. For both systems, the BSA is approximately twice the size of the interstitial space (3nm). In the P123 cylindrical phase, the added BSA changes the structure from HEX to SQR cylindrical micelles. While in the P103 cylindrical phase, the added BSA disrupts the alignment and persistently aligns the micelles (Figure 4.7 (b)). The inconsistent effect that BSA has on the cylindrical phases shows the impact of proteins on the structure and alignment cannot be solely determined from the size of the protein relative to interstitial space. Other factors that may be of importance include the persistence length of the micelles and specific interaction between the BSA and micelles, although the latter should be similar in the two polymer systems.

For the P103 soft solid, the size of the protein is an important factor that affects the structural properties of the cubic and cylindrical phases. The larger protein, BSA, has a diameter greater than the interstitial space, and affects the alignment and polycrystallinity of both phases. However, the smaller protein lysozyme ( $D_H = 4nm$ ) is smaller than or roughly equal to the size of the interstitial space and does not have an appreciable effect on the structural properties and flow mechanism of the cubic and cylindrical phases.

### 4.5 Conclusions

The local structure, phase behavior, and shear alignment of block copolymer soft solids are affected by the addition of nanoparticles in the form of globular proteins. We have characterized the impact of hydrophilic nanoparticles (globular proteins) on the structure (micelle morphology, unit cell structure, and polycrystallinity) of block copolymer soft solids. Oscillatory shear is used to homogeneously align the polycrystalline soft solids into near single crystals, and crystal structure is determined using SANS through multiple projections of the structure. Two different block copolymers with similar architecture and block lengths are investigated (Pluronic<sup>®</sup> P123 and P103); both have an ODT near room temperature and an OOT at a higher temperature from a cubic to a cylindrical phase. In both polymers, the cubic structure aligns to a single crystal with shear and the alignment persists; the addition of the globular protein BSA changes the P123 crystal structure to twinned FCC rather than RCP while for the P103 system the unit cell appears the same, but the polycrystallinity is higher and it is more difficult to form single crystals through shear. At higher temperatures, rod-like micelles hexagonally pack and align in the direction of shear for both polymers. In the P123 cylindrical phase, there is indication of undulations along the length of the micelles suggesting flexibility in the micelles. The addition of BSA drives the hexagonal packing of the cylindrical micelles to a square packing. For the P103 system, the rod-like micelles are not as well organized as in the P123 system. The addition of BSA disrupts the packing and persistently aligns the micelles. This work demonstrates that it is possible to incorporate hydrophilic nanoparticulate material into nanostructured block copolymer soft solids, but the

design space is complex and the nanoparticles can interfere with the shear alignment, induce an alignment, and change the unit cell structure.

## 4.6 References

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# Chapter 5 Impact of structural history on the structural properties and ordering kinetics of cubic structured soft solids

## 5.1 Introduction

For many systems, the temperature defines the structural properties. Thermal changes can induce structural transitions such as an order-disorder transition (ODT) between a disordered liquid and an ordered phase, or an order-order transition (OOT) between two ordered phases with different unit cell structures. In block copolymer melts and solutions, the pathway and ordering kinetics of a transition are system dependent.<sup>1–10</sup> Reported order-order transitions include those between spheres arranged in a face-centered cubic (FCC) and body-centered cubic structure (BCC)<sup>11–13</sup>, lamella (LAM) and hexagonally close packed cylinders (HEX)<sup>2,14,15</sup>, LAM and gyroid<sup>16,17</sup>, gyroid and HEX<sup>18,19</sup>, square packed cylinders and FCC<sup>20</sup>, and HEX and a cubic structure (FCC or BCC).<sup>3–11,20–22</sup> Of the structural parameters previously mentioned, both the unit cell structure and polycrystallinity are particularly sensitive to structural history.<sup>4,7–9,21,23</sup>

The objective of this chapter is to quantify the effect of structural history on the cubic phase of block copolymer soft solids. The polymer systems examined are the same ones used in Chapter 4 and are made from concentrated solutions of either Pluronic<sup>®</sup> P123 or Pluronic<sup>®</sup> P103. In Chapter 4, we examined the impact of processing conditions, specifically high amplitude deformation, on the structural properties of these soft solids in the cubic and cylindrical phases. The deformation does not affect the micelle morphology or unit cell structure, however, the deformation decreases the polycrystallinity to produce a persistently aligned near single crystal.

In this chapter, the structural history is varied by forming the cubic phase through the ODT from a disordered liquid and through the OOT from an aligned cylindrical phase. Rheometry measures the mechanical response of the system during the structural transition, and SANS is used to determine the morphology of the micelles, the micellar unit cell, and polycrystallinity. The samples are macroscopically aligned using high amplitude oscillatory shear to gather improved crystallography as well as information about the flow mechanism of the soft solid. These results show the structural history does not change the micelle shape, the crystalline arrangement of the micelles, or flow mechanism, yet it does impact the polycrystallinity. The cubic phase formed through the OOT is less polycrystalline and forms through an epitaxial transition that requires approximately 20 minutes for completion.

#### 5.2 Material and Methods

The samples are prepared following the procedure in Section 3.3. The total polymer concentration in the samples is 35wt% P123 or 34wt% P103.

Rheology experiments are performed to measure the mechanical response to temperature and applied shear. Samples are loaded according to the protocol in Section 3.4. Rheological temperature sweeps are conducted to measure the magnitude of the complex modulus is measured while heating and cooling the system between 5°C to 45°C. Modulus relaxation experiments use the protocol described in Section 3.4. Thermal transitions from 5°C to 17°C/25°C (P123/P103) and from 45°C to 17°C/25°C are used. At 45°C, high amplitude oscillatory shear (1000%, 5Hz, 3 minutes) is applied, and this is followed by 90 minutes at rest before cooling to 17°C/25°C. After equilibrating at the desired temperature for 50 minutes, high amplitude oscillatory shear (1000%, 5Hz, 3 minutes) is applied.

The Rheo-SANS experiments follow a procedure similar to the relaxation experiment. The system is heated from 5°C to 17°C/25°C and from 45°C to 17°C/25°C. At 45°C, the P123 and P103 samples are sheared using high amplitude oscillations (1000%, 5Hz) for 4 minutes and 15 minutes, respectively, and then allowed to rest for 90 minutes. After the structural transition begins, the samples are equilibrated at 17°C/25°C for 40 minutes. After this equilibration, high amplitude oscillatory shear (1000%, 5Hz) is applied to the P123 and P103 systems for 4 minutes and 15 minutes, respectively. Scattering experiments are conducted 5, 60, and 90 minutes after the cessation of shear.

### **5.3 Results**

The morphology of the micelle, unit cell structure, and phase behavior of these systems are determined using small angle scattering techniques, birefringence, and visual observations (Chapter 4).<sup>10,24</sup> For the P123 soft solid, the structure changes from an isotropic phase made of spherical micelles arranged in a FCC crystal to a birefringent HEX phase.<sup>10</sup> The structure of the P103 soft solid changes from a isotropic phase made of spherical micelles arranged in a BCC crystal to a birefringent HEX phase.<sup>24</sup>

Figure 5.1 demonstrates the thermal response of the magnitude of the complex modulus,  $|G^*|$ , as the P123 and P103 systems are heated and cooled

between 5°C and 45°C. The heating curves are the same as those presented in Figure 4.1; however, Figure 5.1 now includes the cooling curves. The vertical lines represent the structural phase boundaries. Both P123 and P103 systems display similar thermal behavior. At 5°C, the modulus is relatively low, <1Pa. As the system is heated, the modulus rapidly increases by five orders of magnitude to a value of 40-50kPa. Further increasing the temperature causes the modulus to decreases up to an order of magnitude. The cooling curve observes the similar transitions to the heating curve.



Temperature (°C) Temperature (°C) Figure 5.1: Magnitude of the complex modulus as a function of temperature for 35wt% P123 and 34wt% P103 in water. The samples are heated and cooled at a rate of 1°C/min and probed with small amplitude oscillations (0.5%, 1 rad/s). The dotted lines denote temperatures at which the system undergoes an ODT and OOT. Data collected during heating is represented as closed symbols and data collected during cooling is represented as open symbols.

The sharp increase in the modulus indicates an ODT from a disordered viscous liquid to a soft solid with a modulus of tens of kPa. The  $T_{ODT}$  (G'>G") is denoted by the vertical line at 12°C for P123 and 17°C for P103. When observed between two crossed polarizing films, both P123 and P103 systems are isotropic

below 27°C and birefringent between 27°C and 45°C. In these systems, the onset of birefringence indicates a change in the anisotropy of the unit cell structure between an isotropic cubic phase and an anisotropic cylindrical phase (Chapter 4). The  $T_{OOT}$  is 27°C for both systems. Furthermore, similarities between the heating and cooling curves indicate the structural transitions are thermoreversible. The hysteresis between the heating and cooling curves is due to the fact that the structural transition through the OOT is pathway dependent.<sup>4,6,10,22</sup> The modulus of the isotropic soft solid (between  $T_{ODT}$  and  $T_{OOT}$ ) is approximately the same regardless of the thermal history, which suggests the structural history does not affect the structural properties of this isotropic phase.

In this work, we focus on the impact of structural history on the structural properties of the isotropic cubic phase. The cubic phase is examined at 17°C for the P123 system and 25°C for the P103 system. Structural history is varied by forming the cubic phase from a liquid through the ODT via heating from 5°C (liquid) to 17°C/25°C (cubic), and by forming the cubic phase from an aligned cylindrical phase through the OOT via cooling from 45°C (cylindrical) to 17°C/25°C (cubic). The cylindrical phase is aligned using high amplitude oscillatory shear (1000%, 5Hz) at 45°C. Details about the structural properties, flow mechanism, and shear alignment of the cylindrical phase are in Chapter 4.

Figure 5.2 shows the magnitude of the complex modulus as a function of time as the system goes through the different structural transitions. The structural transition begins at time zero when the temperature begins to change. The moduli values measured during the Rheo-SANS experiments are included as close circles

and closely resemble the data collected off-beam. The plots on the left show data collected as the systems go through an ODT from a disordered liquid (5°C) to a cubic soft solid (17°C/25°C). For the P123 and P103 systems, the modulus rapidly increases by five orders of magnitude after the Couette cell reaches the target temperature of 17°C or 25°C. The soft solid forms approximately two minutes after reaching the target temperature. The modulus of the cubic phase formed through the ODT is 36kPa for the P123 system and 34kPa for the P103 system. The plots on the right show data collected as the systems transition through the OOT from an aligned cylindrical phase (45°C) to the cubic phase. For both systems, the modulus gradually increases as temperature decreases, until reaching steady state at approximately 20 minutes. The modulus of the cubic phase formed through the OOT is 16kPa and 32kPa for the P123 and P103 systems. The transitions in the modulus indicates the structural transition from a liquid to cubic phase is rapid and occurs within minutes, whereas the structural change through from a cylindrical phase to a cubic phase requires 20 minutes to reach steady state. The structural history does not significantly affect the modulus of the P103 cubic phase; however, forming the P123 cubic phase through the OOT decreases the modulus.



Figure 5.2: Time dependence of the magnitude of the complex modulus for the P123 and P103 systems as the temperature changes from 5°C (liquid) to  $17^{\circ}C/25^{\circ}C$  (cubic) and from 45°C (cylindrical) to  $17^{\circ}C/25^{\circ}C$  (cubic). The samples are probed with small amplitude oscillations (0.5%, 1 rad/s). Results are for samples containing (a) 35wt% P123 and (b) 34wt% P103 in water. Data collected during the Rheo-SANS experiments are shown by the closed circles.

To quantify the impact of geometry on the heating of the system, Figure 5.3 compares the magnitude of the complex modulus as a function of time for 33wt% P103 and 34wt% P103 in water as the temperature increases from 5°C (liquid) to  $25^{\circ}$ C (cubic). The slight difference between the P103 concentrations should not impact the results. Figure 5.3 (a) shows data collected using the parallel plate geometry while Figure 5.3 (b) shows data collected using the Couette cell. In the parallel plate geometry, Figure 5.3 (a), the temperature is

measured at the bottom plate. For the parallel plate geometry, the soft solid forms (G'>G") at approximately 90 seconds, which is approximately 30 seconds after the bottom plate reaches the  $T_{ODT} = 17^{\circ}$ C. At approximately 100 seconds, temperature reaches 25°C and the modulus of the soft solid immediately reaches a steady state value of 36kPa.



Figure 5.3: Time dependence of the magnitude of the complex modulus when heated from 5°C to 25°C. The samples are probed with small amplitude oscillations (0.5%, 1 rad/s). Results are for (a) 33wt% P103 in water using a parallel plate geometry and (b) 34wt% P103 in water using a Couette cell.

For the Couette cell, the temperature corresponds to the temperature of the heating jacket that encases the cup. In Figure 5.3 (b), the temperature of the jacket reaches the  $T_{ODT}$  at approximately 100 seconds; however, the modulus does not begin to increase until after the rheometer reaches 25°C at 200 seconds and the soft solid does not form until 400 seconds. Over the next 400 seconds, the modulus of the soft solid gradually increases from 10kPa to 30kPa.

In both parallel plate and Couette geometries, there is a lag between soft solid formation and temperature due to heating affects. Heating requires an additional 30 seconds in the parallel plate and an additional five minutes in the Couette cell. This lag is more pronounced in the Couette cell which indicates that heating occurs more slowly in this geometry.

Figure 5.4 shows two-dimensional radial scattering patterns for the cubic phase formed by different structural histories. Scattering patterns are collected 40 minutes after the start of the structural transition. Figure 5.4 (a) shows scattering patterns for the cubic phase formed through the ODT. The scattering patterns for the P123 and P103 systems have a distinct isotropic ring consistent with a powder scattering pattern typically measured for polycrystalline or unaligned systems.



Figure 5.4: Two-dimensional radial scattering patterns for the P123 and P103 systems at rest. Scattering patterns are for (a) the cubic phase formed through the ODT and (b) cubic phase formed through the OOT. Radial scattering for the aligned cylindrical phase ( $45^{\circ}$ C) is included. The radial patterns are collected after the samples are equilibrated at  $17^{\circ}$ C (P123) or  $25^{\circ}$ C (P103) for 40 minutes. The scattering length density of the solvent is 40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O.

Figure 5.4 (b) shows the scattering patterns for the cubic phase formed through the OOT. Scattering for the aligned cylindrical phase are included to provide a reference for the micelle orientation prior to transitioning to the cubic phase (discussed in Figures 4.4 and 4.7). For both P123 and P103 systems, the scattering from the cylindrical phase has two-meridional spots indicating the cylindrical micelles are oriented parallel to the shear direction. After the systems goes through the OOT, the scattering patterns have six distinct Bragg spots. This anisotropy in the scattering intensity indicates the cubic phase is partially aligned. The q position of the primary ring ( $q^*$ ) is provided in Table 5.1. Table 5.1 shows that the value of  $q^*$  is the same for the cubic phase formed through the ODT and OOT, which indicates the micelle size is unaffected by structural history.

	Structural	Powder	At cessation of shear			At rest		
Sample	history (T <sup>o</sup> C)	$q^*(Å^{-1})$	q* (Å <sup>-1</sup> )	$({A}^{-1})$	$(A^{-1})$	q* (Å <sup>-1</sup> )	$({A}^{-1})$	$({A}^{-1})$
P123	ODT/17°C	0.046	0.043	0.071	0.083	0.043	0.071	0.083
	OOT/17°C	0.044	0.042	0.072	0.085	0.042	0.072	0.085
P103	ODT/25°C	0.048	0.044	0.073	0.087	0.045*	0.070*	0.085*
	OOT/25°C	0.048	0.045	0.071	0.088	0.045*	0.070*	0.088*

Table 5.1: Values of q from SANS for the primary  $(q^*)$  and higher order rings. The q values are equivalent to the positions of the isotropic rings or the position of the Bragg spots in the radial patterns. The error of the q\* values is approximately 0.003 Å<sup>-1</sup>. The higher order q values and those obtained from the 1.0m data have a slightly larger error; however, it does not significantly affect the results of the analysis. (\*) indicates values are from scattering collected after 60 minutes at rest.

Figure 5.5 shows two-dimensional radial scattering patterns for 35wt% P123 as the structure transitions from aligned hexagonally close packed cylinders to FCC packed spheres. The scattering patterns are presented in four minute increments, where time zero is the time at which the structural transition begins. Below the scattering patterns is a plot of intensity as a function of azimuthal angle at a value of q\*. This plot clearly shows the evolution of the scattering anisotropy as a function of time. At time zero, the scattering pattern has two-meridional spots

indicating the cylindrical micelles are aligned parallel to the shear direction. After eight minutes, the meridional spots divide into four spots that broaden and shift towards the equator. Two equatorial spots appear after 16 minutes, and by 20 minutes, the system reaches steady state. The time scale of this structural transition is consistent with the rheological data in Figure 5.2. Additionally, the manner in which the scattering intensity evolves suggests the cubic phase is formed through an epitaxial transition from the cylindrical phase.<sup>3,8,9</sup>



Azimuthal angle,  $\phi$  (degree)

Figure 5.5: Two-dimensional radial scattering patterns for the 35wt% P123 as the temperature decreases from  $45^{\circ}$ C (cylindrical) to  $17^{\circ}$ C (cubic). The radial patterns are presented in 4 minute increments between 0 to 20 minutes, where time zero is when cooling begins. A plot of scattering intensity as a function of azimuthal angle at a value of q\* for these scattering patterns is included below. The scattering profiles are shifted vertically for clarity.

The two-dimensional scattering pattern for the cubic phase formed through the OOT for 35wt% P123 (Figure 5.4) is analyzed. Figure 5.6 (a) shows the scattering intensity I(q) at a value of q\* as a function of azimuthal angle for the scattering pattern in Figure 5.4 (b), where the azimuthal angle is the angle from the velocity vector. There are four high-intensity peaks at  $55^{\circ}$ ,  $125^{\circ}$ ,  $235^{\circ}$ , and  $305^{\circ}$  and two low-intensity peaks at  $0^{\circ}$  and  $180^{\circ}$  that correspond to the six spots in the two-dimensional scattering pattern.

To determine if these spots are located at the same q position, a sector analysis is performed by measuring the intensity as a function of q at specific azimuthal angles. Figure 5.6 (b) shows the sector analysis for  $0^{\circ}$  and  $55^{\circ}$ . The Bragg spot that occurs at  $55^{\circ}$  is located at a  $q/q^*$  value of 1 and the Bragg spot at  $0^{\circ}$  is located at a q/q\* value of approximately  $\sqrt{4/3}$ . Since these scattering profiles overlap, SAXS data is included to demonstrate that the difference between the peak positions is significant. The SAXS data for 35wt% P123 in water at 25°C has a primary and secondary peak located at  $q/q^* = 1$  and  $\sqrt{4/3}$ defined by the vertical dashed lines. The position of q\* is consistent with the position of the Bragg spot located at 55°, whereas the position of the secondary peak is consistent with the position of the Bragg spot located at 0°. This scattering pattern is consistent with scattering predicted from the (110) plane of a FCC crystal. Figure 5.6 (c) shows the simulated diffraction pattern with the beam scattering from the (110) plane of a FCC crystal.<sup>25</sup> In the primary ring  $(q/q^* = 1)$ , there are four reflections from the (111) plane located at  $\pm 55^{\circ}$  from the shear

direction. The secondary ring  $(q/q^* = \sqrt{4/3})$  has two reflections from the (200) plane located along the horizontal.



Figure 5.6: Crystallographic analysis of the scattering for the cubic phase formed through the OOT for 35wt% P123 (Figure 5.4 (b)). (a) Scattering intensity as a function of azimuthal angle for q\*. (b) Scattering profiles obtained at the azimuthal angles of  $\phi = 0^{\circ}$  and 55°. Radially averaged I(q) from SAXS for 35wt% P123 in water at 25°C (sample not sheared) is included for comparison. (c) Simulated diffraction pattern with the beam scattering from the (110) plane of a FCC crystal along with the corresponding radial scattering (Figure 5.4 (b)).

The same analysis is performed on scattering from the cubic phase formed

through the OOT for the P103 system in Figure 5.4 (b). Figure 5.7 (a) shows I(q)

at a value of q\* as a function of azimuthal angle and (b) shows the sector analysis conducted at angles where the Bragg spots are located. The six Bragg spots are located at 0°, 55°, 125°, 180°, 235°, and 305°. The sector analysis, Figure 5.7 (b), shows the Bragg spots are positioned at the same q value. This pattern is consistent with scattering from the (110) plane of a twinned BCC crystal. The spots located at  $\pm$  55° with respect to the velocity direction are due to scattering from the (110) plane of a twinned BCC crystal. The equatorial spots could due to scattering from the (112) plane, (110) plane of a non-twinned BCC crystal, or from a persistent super-cooled cylindrical phase.<sup>3,25–27</sup> This scattering pattern has been collected for block copolymer melts and solutions subjected to steady or oscillatory shear.<sup>3,26,28</sup> Additionally, this scattering pattern is a rotation of experimental and theoretical scattering patterns observed for block copolymer melts that form a BCC crystal structure through an OOT via an epitaxial transition from an aligned cylindrical phase.<sup>3,8,29</sup>



Figure 5.7: Crystallographic analysis of the scattering for the P103 cubic phase formed through the OOT (Figure 5.4 (b)). (a) Scattering intensity as a function of azimuthal angle for q\* extracted from the scattering pattern in Figure 5.4 (b). (b) Scattering profiles obtained at the angles of  $\phi = 0^{\circ}$  and 55°.

Application of a high amplitude oscillation is shown to macroscopically align the micellar crystals into a "single crystal" without inducing shear banding (Figure 4.12).<sup>30,31</sup> Figure 5.8 shows the relaxation of the magnitude of the complex modulus after the cessation of a high amplitude oscillatory shear for the P123 and P103 systems. At time zero, the high amplitude shear is stopped. The magnitude of the complex modulus is measured for 90 minutes after the cessation of shear using a fixed strain and frequency of 0.5% and 1 rad/s, low enough to be considered a probe of the structure. The magnitude of the modulus measured before to shear is included for comparison and represented by the symbols on the y-axis. For both systems, application of shear decreases the modulus by up to

10kPa with no recovery over time. For the P123 system, the modulus of the cubic phase formed through the OOT has a lower modulus than when formed through the ODT before prior to and after the application of shear, suggesting thermal history may affect the alignment of the P123 cubic phase. For the P103 system, the modulus of the cubic phase appears uninfluenced by structural history or shear. Furthermore, the fact that the modulus after shear is constant with time suggests the shear alignment is persistent.



Figure 5.8: Magnitude of the complex modulus as a function of time after cessation of high amplitude oscillatory shear for the cubic phase formed by different structural histories. Results are for samples containing 35wt% P123 and 34wt% P103 in water. The symbols on the left at time zero correspond to the value of  $|G^*|$  measured immediately before shear for the cubic phase formed through the ODT ( $\bullet$ ), and for the cubic phase formed through the OOT ( $\circ$ ).

Examination of the shear aligned structure provides improved crystallography of the structure as well as information regarding the impact of structural history on the flow mechanism. Figure 5.9 shows two-dimensional scattering patterns for the cubic phase after the cessation of shear. As in the Chapter 4, SANS data is collected for 5 minutes and is taken 5 minutes after the cessation of shear ("cessation of shear") and after 60 or 90 minutes at rest ("rest").

Scattering is collected at 3.5m and 1.0m sample-to-detector distances. Table 5.1 tabulates the q values for the primary and higher order rings in the radial scattering patterns.

Figure 5.9 (a) shows scattering patterns for the P123 system in the cubic phase at 17°C formed by different structural histories after the cessation of shear. For the cubic phase formed through the ODT, the radial scattering collected at the cessation of shear has six equidistant Bragg spots in both the primary and higher order rings. The symmetry of the radial scattering pattern is maintained at rest indicating the shear alignment is persistent. For the tangential pattern, the inner ring ( $q^* = 0.045 \text{Å}^{-1}$ ) has two Bragg spots on the equator with smeared off-axis spots. For the cubic phase formed through the OOT, the radial scattering collected at the cessation of shear and at rest has clearly defined rings, with each ring having six equidistant spots. The persistence of this radial scattering pattern is discattering pattern is maintained. The tangential pattern is similar to that cubic phase formed through the ODT and has two equatorial spots and smeared off-axis spots in the primary ting ( $q^* = 0.045 \text{Å}^{-1}$ ).

For the P123 system, scattering patterns of the cubic phase formed by the different structural histories appear almost identical after the cessation of shear. The radial patterns have the same symmetry with Bragg spots located at  $q/q^* = 1$ ,  $\sqrt{8/3}$ , and  $\sqrt{11/3}$ . The radial and tangential patterns are consistent with scattering simulated for a random close packed (RCP) structure made of spherical micelles, with the close-packed (111) plane aligned in the velocity direction.<sup>31–34</sup> The overall semblance between the scattering patterns indicates the shear aligned

structure, flow mechanism, and persistence of the aligned state are not affected by structural history, which is opposite of the mechanics shown in Figure 5.8.



Figure 5.9: Two-dimensional scattering patterns for the P123 and P103 cubic phases formed through the ODT and OOT after the cessation of high amplitude oscillatory shear (5Hz, 1000%). Scattering patterns are for (a) 35wt% P123 and (b) 34wt% P103 after the cessation of shear. The scattering length density of the solvent is 40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O. Radial and tangential patterns are collected after 5 min and 60 min or 90 min at rest at a sample-to-detector distance of 3.5m or 1.0m.

Figure 5.9 (b) shows scattering patterns for the P103 system in the cubic phase at 25°C after the cessation of shear. Radial scattering for the cubic phase formed through the ODT at the cessation of shear has six equidistant spots in the

primary and higher order rings. The symmetry and q position of the spots remains unchanged after 60 minutes at rest which indicates the alignment is persistent. The tangential scattering pattern for the cubic phase formed through the ODT has two meridional spots and six equidistant spots in the primary ring ( $q^* = 0.048 \text{Å}^{-1}$ ). For the cubic phase formed through the OOT, the radial pattern has six equidistant spots in the primary and higher order rings. These Bragg spots appear smeared in comparison to the scattering collected for the cubic phase formed through the ODT. The symmetry of the radial pattern is maintained at rest indicating the alignment is persistent. For the tangential pattern, the primary ring ( $q^* = 0.047 \text{Å}^{-1}$ ) does not have distinct Bragg spots.

For the P103 system, radial scattering patterns for the cubic phase formed by different structural histories (Figure 5.9 (b)) have the same symmetry and q positions. The q position of the rings are tabulated in Table 5.1 and are located at  $q/q^* = 1, \sqrt{3}$ , and  $\sqrt{4}$ . These radial patterns are consistent with scattering from the (111) plane of a BCC crystal, or with the (111) plane aligned in the shear direction.<sup>26,30</sup> Since the relative orientation of the shear aligned state is the same, structural history does not appear to affect the flow mechanism of the cubic phase in the P103 system.

It is important to note the difference in the anisotropy of the scattering patterns. The radial scattering for the cubic phase formed through the OOT appears to have smeared Bragg spots and greater powder scattering in contrast to scattering for the cubic phase formed through the ODT. Figure 5.10 shows the scattering intensity as a function of azimuthal angle at a value of q\* for the radial
patterns in Figure 5.9 (b) to highlight the differences in the anisotropy. The cubic phase formed through the ODT has six equidistant high-intensity peaks, with the peaks at 90° and 270° having greater intensity. The cubic phase formed through the OOT has six equidistant peaks of equal intensity, which have relatively low intensity compared to the scattering intensity of the cubic phase formed through the ODT. This smearing of the Bragg spots indicates the cubic phase formed through through the OOT is more difficult to align.



Azimuthal angle,  $\phi$  (degree)

Figure 5.10: Scattering intensity as a function of azimuthal angle at a value of  $q^*$  for the scattering patterns for 34wt% P103 in Figure 5.9 (b) at 5 minutes after the cessation of shear.

The impact of structural history on the anisotropy of the scattering pattern is even more notable in the tangential scattering. Tangential scattering for the cubic phase formed through the ODT has distinct Bragg spots that are consistent with scattering from the (111) and (112) planes of a BCC crystal (Figure 4.9). However, tangential scattering for the cubic phase formed through the OOT lacks distinct Bragg spots, signifying a poorly aligned or polycrystalline system. This clearly shows that structural history impacts the polycrystallinity and shear-alignment of the system; however, this is not depicted by the mechanical relaxation in Figure 5.8.

To show the impact of thermal history and applied shear on the homogeneity of the alignment within the gap, Figure 5.11 shows scattering in the 1-2 direction at several positions in the gap. The 1-2 scattering patterns are for the P123 cubic phase formed through the OOT before and after the cessation of shear. A plot of intensity as a function of azimuthal angle at a value of  $q^*$  is included to highlight the differences in the scattering patterns. In Figure 5.11 (a), scattering near the moving wall has two peaks at approximately  $0^\circ$  and  $180^\circ$ , while scattering at the center and near the stationary wall has six peaks. Since the position of the peaks is dependent on the gap position, the alignment is not homogenous throughout the gap.

In Figure 5.11 (b), the scattering patterns appear the same at each gap position. Each pattern has two higher intensity equatorial spots and four lower intensity off-axis spots. The consistency of the spot positions indicates the orientation of the shear aligned structure is homogenous throughout the gap.



Figure 5.11: 1-2 scattering for 35wt% P123 in 100% D<sub>2</sub>O collected near the moving wall, gap center, and outer stationary wall. Two-dimensional scattering patterns are for cubic phase formed through the OOT at 17°C for 35wt% P123 (a) before and (b) after the cessation of shear.

## **5.4 Discussion**

The concentrated block copolymer solutions form a soft solid made from spherical micelles packed into a cubic crystalline lattice. Although P123 and P103 form soft solids with different unit cell structures, structural history impacts these systems in the same manner. Temperature induced structural transitions manipulate the structural history of the cubic phase in the soft solid, but do not greatly impact the modulus of the cubic phase (on the order of tens of kPa in Figures 5.1 and 5.2). The micelle morphology, unit cell structure, and flow mechanism of the cubic phase are also unaffected by structural history (Figures 5.4 and 5.9). However, the ordering kinetics of the cubic phase is pathway dependent; the ODT produces a cubic phase on the order of minutes while the OOT produces a cubic phase in 20 minutes. Additionally, the structural history significantly impacts the polycrystallinity of the soft solid. To quantify the changes in the polycrystallinity, a powder fraction ( $\phi_p$ ) is estimated from the scattering intensity.<sup>31</sup> The  $\phi_p$  is estimated by taking the dividing the minimum intensity by the average intensity of the powder scattering (scattering collected for the unaligned system) at a value of q\*

$$\phi_{\rm p} = \frac{(I_{\rm min}(q^*) - I_{\rm bkg})}{(I_{\rm pwdr}(q^*) - I_{\rm bkg})}.$$
(5.7)

Decreasing values of  $\phi_p$  correspond to a decrease in the polycrystallinity. A  $\phi_p = 1$  indicates the system is a powder or polycrystalline while a  $\phi_p = 0$  indicates the system is a perfect single crystal. The  $\phi_p$  values for the cubic phase before and after shear are tabulated in Table 5.2. Large values of  $\phi_p$  (>0.9) correspond to the powder scattering patterns for the polycrystalline cubic phase formed through the ODT in Figure 5.4 (a). Forming the cubic phase through the OOT increases the anisotropy of the scattering intensity and decreases  $\phi_p$  of the P123 and P103 systems (Figure 5.4 (b)). After the application of shear,  $\phi_p$  approaches zero and the scattering patterns have distinct Bragg spots, in Figure 5.9, indicative of a macroscopically aligned cubic phase. The structural history affects the  $\phi_p$  of the shear aligned P103 cubic phase but not the P123 system.

	Powder fraction $(\phi_p)$				
	Cubic (ODT)		Cubic (OOT)		
Sample	Before	After	Before	After	
35wt% P123	0.94	0.09	0.45	0.07	
34wt% P103	0.96	0.10	0.54	0.19	

Table 5.2: Powder fraction  $\phi_p$  for the cubic phase formed through the ODT and OOT before and after the application of shear. A  $\phi_p = 1$  indicates the system is polycrystalline while a  $\phi_p = 0$  indicates the system is a single crystal. The after shear value is calculated using the scattering collected 5 minutes after the cessation of shear.

In addition to decreasing the polycrystallinity of the formed cubic phase, the OOT forms a cubic structure with a specific relative orientation. This alignment is postulated to be a result of an epitaxial transition from the cylindrical to cubic phase, with the alternative being that there is an intermediate disordered liquid-like phase.<sup>1,3–9,23</sup> The fact that the system remains solid-like with a modulus on the order of kPa and the cubic phase is aligned after the OOT supports the idea of an epitaxial transition (Figures 5.2 and 5.4). Additionally, an epitaxial transition in the P123 system is confirmed since the scattering patterns do not exhibit a powder pattern during the OOT (Figure 5.5).

The epitaxial transition between HEX and BCC has been well studied in block copolymer solutions and melts.<sup>3,8,9,26,29</sup> In the literature, the proposed mechanism is that the cylindrical micelles undulate until they eventually pinch off into spheres, where the cylindrical axis coincides with the [111] direction of the BCC crystal.<sup>3,9,29</sup> The resulting structure is a twinned BCC crystal aligned with the (110) plane parallel to the shear direction.<sup>3,6,8</sup> For the HEX to FCC epitaxial transition, the cylindrical axis corresponds to the [110] direction of the FCC crystal, or the (110) plane is parallel to the gradient direction.<sup>13,22,23</sup>

The relative orientations of the P123 and P103 cubic phases formed through the OOT are different than those reported in literature. For the P123 system, the FCC crystal is oriented with the (110) plane parallel to the shear direction rather than parallel to the gradient direction.<sup>9,22,23</sup> Based on the radial scattering (Figure 5.4 (b)) and 1-2 scattering collected near the moving wall (Figure 5.11 (b)), it is predicted the cylindrical axis corresponds to the [112] direction of the FCC crystal. For the P103 system, the scattering pattern collected (Figure 5.4 (b)) is a 90° rotation of the one typically displayed and suggests that there is a persistent cylindrical phase present. This rotation suggests the [112] direction of the BCC crystal is coincident with the cylindrical axis.<sup>3,8,29</sup> Additional projections of the crystal structure are required to verify these predictions.

Application of high amplitude oscillatory shear is another method to control the relative orientation of the crystalline structure. For the P123 system, the applied shear changes both the relative orientation and the stacking of the hexagonally close packed layers of micelles. The P123 cubic phase formed through the OOT changes from a pure FCC stacking with the (110) plane parallel to the shear direction, to having a RCP stacking with the (111) plane parallel the shear direction after the cessation of shear (Figures 5.6 and 5.9). This change from FCC to RCP stacking has been observed for other Pluronic<sup>®</sup> solutions and is caused by the decorrelation of close packed layers by the applied shear.<sup>33</sup> The orientation of the P103 cubic phase formed through the OOT changes from

having the (110) planes to the (111) planes of the BCC crystal being parallel to the shear direction. The change in the orientation and polycrystallinity of the system do not greatly impact the magnitude of the modulus (Figure 5.8). The relative orientation of the shear aligned structure is also unaffected by structural history.

### **5.5 Conclusions**

This work demonstrates how processing conditions, specifically thermal history, affect the structural properties and flow mechanism of block copolymer soft solids. The cubic phase of these soft solids is made of spherical micelles arranged into a cubic crystalline lattice (FCC or BCC). The structural history of the cubic phase is controlled by temperature. The cubic structure is formed by heating the system from a disordered liquid through the ODT, or by cooling the system from an aligned cylindrical soft solid through the OOT. The structural transition through the ODT occurs within minutes while the structural transition through the OOT requires approximately 20 minutes.

Variations in the structural history do not change the spherical morphology of the micelle, the unit cell structure, or the flow mechanism of the cubic phase. However, the polycrystallinity and relative orientation of the cubic structure can be controlled by manipulating the structural history and application of shear. Forming the cubic phase through the OOT decreases the polycrystallinity and preferentially aligns the cubic phase (FCC or BCC) with the (110) plane parallel to the shear direction. This alignment and specific orientation of the cubic phase is a result of an epitaxial transition from the cylindrical phase. However, the relative orientation of the cubic structure differs from those predicted and observed for other block copolymer melts and solutions. Application of shear further decreases the polycrystallinity and changes the relative orientation of the cubic phase such that the (111) plane is parallel to the shear direction. Overall, this work highlights the significance of structural history for handling and processing of these materials.

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Chapter 6 Impact of added nanoparticles on the structural transitions in block copolymer soft solids

## 6.1 Introduction

The block copolymer materials used for particle templating may undergo structural transitions between an ordered and a disordered phase (ODT), or between two different ordered phases (OOT).<sup>1–13</sup> Often, these structural transitions are temperature-induced, thermoreversible, and pathway dependent. Tuning the structural history will alter the polycrystallinity of the system, the relative orientation of the unit cell structure, and the kinetics of the transition.<sup>5,11–17</sup> However, the impact of formulation, specifically the addition of particles, on the structural transitions is not well understood. The addition of nanoparticles has been shown to affect the temperature at which an ODT or OOT occurs, as well as the unit cell structure.<sup>18,19</sup>

This chapter aims to provide new insight on the impact of added nanoparticles on these structural transitions. The systems studied are the same as those described in Chapter 4; globular proteins (BSA or lysozyme) are added to soft solids made from concentrated solutions of Pluronic<sup>®</sup> P123 and Pluronic<sup>®</sup> P103. The previous chapters show the structure of the soft solid changes from a disorder liquid at low temperatures (~5°C), to a soft solid of spherical micelles arranged in a BCC or FCC crystal near ambient temperatures, to a soft solid made of hexagonally close packed cylindrical micelles (HEX) at elevated temperatures (45°C). In Chapter 5, the thermoreversible nature of the phase behavior is used to examine the effect of structural history on structural properties of the cubic phase.

The results show that the morphology of the micelle, the cubic structure, and flow mechanism of the system are not affected by structural history while the polycrystallinity and ordering kinetics of the cubic phase are dependent.

This chapter aims to determine how the added protein impacts the ordering kinetics and properties of the ODT and OOT as well as the impact of added proteins on the structural properties of the formed cubic phase. The structural and shear histories employed are the same as those used to probe the neat systems (without protein) in Chapter 5. Rheology and SANS are used to measure the measure the structural and mechanical response of the soft solid. In these composite systems, the structural history does not affect the micelle morphology, the unit cell structure, or flow mechanism of the cubic phase. The OOT occurs via an epitaxial transition that requires up to 30 minutes and produces a partially aligned cubic phase. Compared to the neat system (without proteins), the added protein decreases the alignment of the cubic phase formed through the OOT and increases the time required for the completion of the ODT, but the added protein does not affect the cubic phase formed through the ODT.

### 6.2 Materials and Methods

The samples are prepared following the procedure in Section 3.3. For the rheometric experiments, samples are loaded according to the protocol in Section 3.4. The temperature sweeps and modulus relaxation experiments are the same as those performed in Section 5.2. At 45°C, the samples are sheared using high amplitude oscillatory shear and then rested for 90 minutes before being cooled;

the P103 system with BSA uses a preshear of 5Hz and 500% for 5 minutes while the remaining systems use a preshear of 5Hz and 1000% for 3 minutes. After equilibrating at 17°C/25°C for 50 minutes, P103 system with BSA is sheared using 5Hz and 2500% for 3 minutes, and the remaining systems use 5Hz and 1000% for 3 minutes.

The Rheo-SANS experiments follow the thermal procedures in Section 3.5.2 and Section 5.2. At 45°C, the P103 system with BSA is aligned using 5Hz and 500% for 8 minutes while the remaining systems use 5Hz and 1000% for 4 minutes. After the systems are equilibrated at 17°C/25°C, the P103 system with BSA is sheared using 5Hz and 2500% for 4 minutes while the remaining systems use 5Hz and 1000% for 4 minutes.

### 6.3 Results

Figure 6.1 shows the thermal response of the magnitude of the complex modulus  $|G^*|$  for the P123 and P103 systems with added proteins. The P123 and P103 composite systems exhibit similar transitions to the neat systems (without protein) in Figure 5.1. At 5°C, the modulus is low and <1Pa. As the temperature rises, the modulus increases by approximately five orders of magnitude to approximately 40kPa and then gradually decreases. At 45°C, modulus has decreased by three orders of magnitude for the P123 and P103 systems with BSA and by approximately one order of magnitude for the P103 system with lysozyme. The cooling curves exhibit the same general trends. However, there is a clear hysteresis between the heating and cooling curves that is more pronounced for the P123 system with added BSA.



Figure 6.1: Thermal response of the magnitude of the complex modulus for 35wt% P123 or 35wt% P103 with 3wt% BSA or lysozyme in water. The samples are heated or cooled at a rate of 1°C/min and probed with small amplitude oscillations (0.5%, 1 rad/s). The dotted lines denote temperatures at which the systems with BSA undergo an ODT and OOT. Data collected during heating is represented by closed symbols and data collected during cooling is represented by open symbols.

The vertical lines represent temperatures at which structural transitions occur for the composite systems with added BSA. The  $T_{ODT}$  (G'>G") is 16°C for the P123 system with BSA, 19°C for the P103 system with BSA, and 17°C for the P103 system with lysozyme. When observed between two crossed polarizing films, the systems transition from being isotropic to birefringent at elevated temperatures. For these particular systems, the onset of birefringence indicates an OOT in the unit cell structure between a cubic (isotropic) and cylindrical structure (birefringent) (Chapter 4).<sup>17,20</sup> The order-order transition temperature ( $T_{OOT}$ ) is defined as the temperature that birefringence onsets, which is 27°C for the P123 system, between 25°C and 26°C for the P103 system with BSA, and 26°C for the P103 system with lysozyme. The hysteresis between the heating and cooling curves indicates the structural transition through the OOT is pathway

dependent.<sup>10,15,17</sup> Regardless of thermal history, the modulus of the isotropic soft solid remains on the order of tens kPa, suggesting the structural properties of the isotropic cubic phase are independent of thermal history.

The isotropic cubic phase is examined at 17°C for the P123 system and 25°C for the P103 systems. To study the impact of structural history, the cubic phase forms from a liquid through the ODT by heating from 5°C to 17°C/25°C and from an aligned cylindrical phase through the OOT by cooling from 45°C to 17°C/25°C. These are the same structural histories used to study the neat system (without proteins) in Chapter 5. Details about the alignment and structure of the cylindrical phase have been presented in Chapter 4. For the P123 system with BSA, the cylindrical micelles organize in a square configuration (SQR) and align parallel to the shear direction. For the P103 system, the added BSA disrupts the hexagonal packing and the cylindrical micelles align in the vorticity direction, whereas the P103 system with lysozyme has a HEX structure with the micelles aligned parallel to the shear direction.

Figure 6.2 shows the mechanical response of the system as it goes through the different structural transitions. At time zero, the structural transition (temperature change) begins. Moduli values measured during the Rheo-SANS experiments are included as open symbols. The plots on the left show the magnitude of the modulus as the system transition from a liquid (5°C) to the cubic phase (17°C/25°C). For both P123 and P103 systems with added proteins, the modulus increases by five orders of magnitude after the Couette cell reaches 17°C or 25°C. The formation of the soft solid occurs two to five minutes after the Couette cell reaches the cubic temperature. This lag is a due to heating affects associated with the geometry chosen (Figure 5.3). The plots on the right show the magnitude of the modulus as the system goes through an OOT from an aligned cylindrical phase to a cubic phase. As the temperature decreases from 45°C, the modulus remains relatively constant. Once the temperature reaches 17°C or 25°C, the modulus gradually increases before reaching steady state between 20 minutes and 40 minutes. The structural history does not impact the modulus of the cubic phase for the P123 system with BSA or the P103 system with lysozyme. For the P103 system with BSA, the cubic phase formed through the OOT has a lower modulus. These moduli values agree fairly well with the values measured during the Rheo-SANS experiments.



Figure 6.2: Magnitude of the complex modulus as the temperature changes from  $5^{\circ}$ C (liquid) to  $17^{\circ}$ C/ $25^{\circ}$ C (cubic) and from  $45^{\circ}$ C (cylindrical) to  $17^{\circ}$ C/ $25^{\circ}$ C (cubic). The samples are probed with small amplitude oscillations (0.5%, 1 rad/s). Results are for samples containing (a) 35wt% P123 with 3wt% BSA and (b) 35wt% P103 with 3wt% BSA or lysozyme in water. Moduli values measured during the Rheo-SANS experiments for samples with 3wt% BSA ( $\circ$ ) and with 3wt% lysozyme ( $\Box$ ) are included. The samples used in the Rheo-SANS experiments have a solvent of 40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O.

Figure 6.3 shows two-dimensional radial scattering patterns for the cubic phase formed through the ODT and OOT. The scattering length density of the solvent is matched to the protein (40.7mol%  $D_2O$ :59.3mol%  $H_2O$ ). Figure 6.3 (a) shows scattering for the cubic phase formed through the ODT. These patterns have an isotropic ring that is consistent with powder scattering from polycrystalline systems.



Figure 6.3: Two-dimensional powder scattering patterns for the composite systems at rest. Scattering patterns are for (a) the cubic phase formed through the ODT and (b) cubic phase formed through the OOT. The radial patterns are collected after the samples equilibrate at  $17^{\circ}$ C (P123) or  $25^{\circ}$ C (P103) for 40 minutes. The scattering length density of the solvent (40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O) is matched to the protein.

Figure 6.3 (b) shows the scattering patterns for the cubic phase formed through the OOT. These scattering patterns are collected 40 minutes after the start of the structural transition. Radial scattering for the cylindrical phase is included to provide a reference of the cylindrical micelle orientation prior to the OOT. In the cylindrical phase, scattering for the P123 system with BSA and P103 system with lysozyme have two meridonal spots indicating the micelles are parallel to the velocity direction while scattering for the P103 system with BSA has two equatorial spots indicating the micelles are parallel to the vorticity direction. After

the OOT, the scattering patterns for the cubic phases have six Bragg spots in the primary ring. This anisotropy in the scattering intensity indicates the OOT forms a partially aligned cubic phase. The q position of the primary ring (Table 6.1) is the same for the cubic phase formed through the ODT and OOT indicating the micelle size is unaffected by the structural history.

	Structural Powde		At cessation of shear			At rest		
Sample	history (T <sup>o</sup> C)	$q^*(A^{-1})$	q* (Å <sup>-1</sup> )	q <sub>2</sub> (Å <sup>-1</sup> )	$({A}^{-1})$	q* (Å <sup>-1</sup> )	$(\text{\AA}^{-1})$	q <sub>3</sub> (Å <sup>-1</sup> )
P123	ODT/17°C	0.045	0.042	0.068	0.082	0.043	0.069	
+BSA	OOT/17°C	0.044	0.042	0.069	0.082	0.043	0.069	
P103	ODT/25°C	0.048	0.047			$0.047^{+}$		
+BSA	OOT/25°C	0.047	0.047			0.047		
P103 +LYS	ODT/25°C	0.048	0.045	0.072	0.086	0.045	0.072	0.086
	OOT/25°C	0.048	0.045	0.070	0.088	0.045	0.070	0.088

Table 6.1: Values of q from SANS for the primary  $(q^*)$  and higher order rings. The q values are equivalent to the positions of the isotropic rings or the position of the Bragg spots in the radial patterns. The error is approximately 0.003 Å<sup>-1</sup> for the q\* values and slightly greater for the higher order rings. (<sup>+</sup>) indicates values are from scattering collected after 6 hours at rest.

Figure 6.4 shows the scattering intensity as a function of azimuthal angle to highlight the presence of Bragg spots in the primary ring for the scattering patterns in Figure 6.3 (b). Scattering for the P103 system with lysozyme is similar to the scattering collected for the P103 neat system in Figure 5.4; the peaks have the same anisotropy and are located at the same angles (0°, 55°, 125°, 180°, 235°, 305°) and q position. This shows the added lysozyme does not impact the relative orientation of the cubic phase, which is a twinned BCC crystal with the (110) plane parallel to the velocity direction.

For the systems with BSA, the Bragg spots are less discernable and the peaks have relatively low amplitude which makes it difficult to identify the relative orientation of the micelle crystal. Compared to the scattering from the neat system in Figure 5.4, the Bragg spots are located at similar azimuthal angles, suggesting the added BSA does not affect the relative orientation of the P123 and P103 soft solids.



Azimuthal angle  $\phi$  (degree)

Figure 6.4: Scattering intensity  $(I(q^*,\phi))$  as a function of azimuthal angle at a value of q<sup>\*</sup> for the scattering patterns in Figure 6.3 (b) for the cubic phase formed through the OOT. The scattering profiles are shifted vertically for clarity.

Figure 6.5 shows the temporal evolution of the radial scattering pattern as the systems transitions from the cylindrical to cubic phase through the OOT. The scattering patterns are presented in 4 or 6 minute increments, where time zero is when the structural transition begins. The P123 system with BSA and the P103 system with lysozyme exhibit the same trend even though they have different cylindrical structures. At time zero, the scattering pattern has two meridional spots. The meridional spots divide and migrate towards the equator after eight minutes, and equatorial spots emerge around 16 minutes before the system reaches steady state at 20 minutes. The P103 system with BSA exhibits different behavior; initially the scattering pattern has two equatorial spots that persist for 18 minutes. Four off-axis spots appear after 24 minutes but the system does not reach steady state until 30 minutes. The timescale of the structural transition is consistent with the timescale of the mechanical response (Figure 6.2). The evolution of the scattering pattern is consistent with an epitaxial transition between a cubic and cylindrical phase and evolve in a similar fashion to the neat system (Figure 5.5).<sup>5,12,13</sup>

### 35wt% P123 + 3wt% BSA







# 35wt% P103 + 3wt% LYS



Figure 6.5: Two-dimensional scattering patterns collected as the structure transitions from cylindrical to cubic. The radial patterns are presented in 4 or 6 minute increments, where time zero is when the structural transition begins. The scattering length density of the solvent (40.7mol%  $D_2O$ :59.3mol%  $H_2O$ ) is matched to the protein.

As done in the previous chapters, a short application of high amplitude oscillation is used to macroscopically align the micellar crystal into a single crystal.<sup>14,21</sup> Figure 6.6 shows the relaxation of the magnitude of the complex modulus after the cessation of shear where shear stops at time zero. The modulus of the powder state (prior to shear) is represented by the symbols on the y-axis. For P123 system with BSA and P103 system with lysozyme, the modulus slightly drops after the cessation of shear. The modulus of the P123 system with BSA partially recovers with time, while the modulus of the P103 system with lysozyme is largely insensitive to the time and structural history. Additionally, the moduli of the powder and aligned states are approximately the same.



Figure 6.6: Magnitude of the complex modulus as a function of time for cubic phase after the cessation of high amplitude oscillatory shear. Results are for samples containing (a) 35wt% P123 with 3wt% BSA, and (b) 35wt% P103 with 3wt% BSA or lysozyme in water. The symbols on the left correspond to the value of  $|G^*|$  measured immediately before shear.

For the P103 system with added BSA, the applied shear causes the modulus to decrease by approximately two orders of magnitude and slowly recover over the next 30 minutes. After 90 minutes, the modulus of the cubic

phase formed through the ODT is lower than the cubic phase formed through the OOT, suggesting the cubic phase formed through the ODT is easier to align.

Overall, the fact that the modulus displays the same trend regardless of structural history, suggests the shear-aligned cubic phases will display the same structural properties. The shear alignment of the cubic phase formed through the ODT is discussed in detail in Chapter 4. The results in Chapter 4 show that both composite systems with BSA exhibit transient behavior after the cessation of shear while the P103 system with lysozyme aligns into a persistent single crystal.

To determine the impact of structural history on the shear alignment on the nanostructure, multiple projections of the crystal structure are gathered using Rheo-SANS. For consistency, scattering is collected 5 minutes after the cessation of shear ("cessation of shear") and after 90 minutes at rest ("at rest"). Figure 6.7 shows scattering patterns for the cubic phase collected after the cessation of shear. The q values for the primary and higher order rings in the radial patterns are listed in Table 6.1, and are relatively insensitive to structural history. For the three composite systems examined, the scattering patterns for the cubic phase formed through the ODT and OOT appear almost identical. This demonstrates the structural history does not impact the shear alignment and flow behavior of the cubic phase.



Figure 6.7: Two-dimensional scattering patterns for the cubic phase formed through the ODT and OOT after the cessation of shear. Scattering patterns are for (a) 35wt% P123 with 3wt% BSA at  $17^{\circ}$ C, (b) 35wt% P103 with 3wt% BSA at  $25^{\circ}$ C, and (c) 35wt% P103 with 3wt% lysozyme at  $25^{\circ}$ C. The scattering length density of the solvent (40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O) is matched to the protein. Radial and tangential patterns are collected 5 and 90 minutes after the cessation of shear unless otherwise noted.

Radial scattering for the P123 system with BSA, Figure 6.7 (a), has six equidistant spots in the inner and higher order rings at the cessation of shear. These rings are located at  $q/q^* = 1$ ,  $\sqrt{8/3}$ , and  $\sqrt{11/3}$ . The tangential scattering has three rings at  $q/q^* = 1$ ,  $\sqrt{4/3}$ , and  $\sqrt{8/3}$ ; the primary ring has two equatorial spots along with four spots  $\pm 70^{\circ}$  from the horizontal, the secondary ring has four spots  $\pm 55^{\circ}$  from the horizontal, and the third order ring has four spots  $\pm 35^{\circ}$  from the horizontal. The radial and tangential scattering patterns are consistent with scattering from a twinned FCC crystal with the close packed (111) plane parallel to the shear direction.<sup>21–23</sup> At rest, the Bragg spots in the radial scattering appear to have divided into multiple spots. This change in the anisotropy indicates the alignment is not persistent and suggests the micellar crystals are reorienting with time. This slow transition is believed to be the cause of the gradual increase in the modulus in Figure 6.6.

For the P103 system with BSA, the radial scattering in Figure 6.7 (b) has six equidistant spots in the primary ring at the cessation of shear. This radial pattern is maintained for at least 90 minutes, demonstrating this alignment is persistent. The tangential pattern has an isotropic ring indicating poorly alignment of the system.

For the P103 system with lysozyme, the radial scattering in Figure 6.7 (c), has clearly defined rings located at  $q/q^*$  values of 1,  $\sqrt{3}$ , and  $\sqrt{4}$  that each contain six equidistant Bragg spots. Additionally, there are four lower-intensity spots in the primary ring located  $\pm 40^\circ$  from the horizontal that become more distinguishable with time. The increasing presence of the lower-intensity spots

suggests the relative orientation of the micellar crystal is changing. Overall, the six equidistant spots in the radial pattern are consistent with scattering from the (111) plane of a BCC crystal, and the tangential scattering is consistent with scattering from the (112) and (111) planes of a BCC crystal.<sup>13,14,24</sup>

Figure 6.8 shows radial scattering for the P103 system with BSA in the cubic phase during and immediately after the cessation of shear. The scattering is presented in one minute increments for the first 5 minutes after the cessation of shear. The cubic phase formed through the ODT and OOT exhibit the same clear transitions in the scattering; during shear the scattering has two meridional spots that transition to 6 equidistant spots after 3 minutes at rest. The timescale for transition occurs on the same timescale as the relaxation of the modulus (Figure 6.6 (b)). Based on this transient behavior and value of q\*, it is proposed that the applied shear shifts the phase boundary such that the system is in a HEX phase during shear. Once shear stops, the phase boundary reverts and returns the system to a primarily cubic phase. Shifting the phase boundary requires minutes.



Figure 6.8: Two-dimensional scattering patterns for 35wt% P103 with 3wt% BSA collected during and directly after the cessation of shear. The scattering length density of the solvent (40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O) is matched to the protein. Scattering patterns after shear are presented in 1 minute increments for the first 5 minutes.

# 6.4 Discussion

The added protein does not inhibit the structural transitions of the polymer solution. The soft solid forms a cubic phase by means of a temperature induced ODT or OOT. The micelle morphology, unit cell structure, shear alignment, and mechanics of the cubic phase are unaffected by the structural history, yet the polycrystallinity of the formed cubic phase is sensitive. This sensitivity is revealed by the dependence of the scattering anisotropy on the structural history (Figure 6.3). A powder fraction ( $\phi_p$ ) is estimated to using equation (5.1) to quantify the volume fraction of the system that is polycrystalline, or that deviates from a perfect "single crystal."<sup>21</sup>

The values of  $\phi_p$  in Table 6.2 show the cubic phase formed through the ODT is polycrystalline ( $\phi_p > 0.95$ ). However,  $\phi_p$  decreases to a value between 0.6 and 0.8 when formed through the OOT, with the P103 system with BSA having the greatest  $\phi_p$ . The  $\phi_p$  further decreases after the cessation of high amplitude shear; the P123 system with BSA and the P103 system with lysozyme have  $\phi_p < 0.1$  indicating these soft solids are macroscopically aligned while the P103 system with BSA has a  $\phi_p$  (~0.6) consistent with a partially aligned system. The polycrystallinity and relative orientation of the cubic phases formed via the ODT and OOT are identical after the short application of shear.

	Powder fraction $(\phi_p)$				
	Cubic	(ODT)	Cubic (OOT)		
Sample	Before	After	Before	After	
P123 + BSA	0.97	0.08	0.65	0.08	
P103 + BSA	0.96	0.59	0.79	0.63	
P103 + LYS	0.97	0.09	0.60	0.09	

Table 6.2: Powder fractions for the cubic phase formed through the ODT and OOT before and after the application of shear. A  $\phi_p = 0$  indicates the system is a single crystal while a  $\phi_p = 1$  indicates the system is a polycrystalline. The  $\phi_p$  after shear is calculated using the radial scattering collected 5 minutes after the cessation of shear.

These composite systems display many similarities and differences to the neat systems. Similarities include the effect structural history has on the polycrystallinity, and the lack of effect it has on micelle morphology, unit cell structure, flow mechanism, and shear alignment. Additionally, the added protein does not impact the ODT; the ODT of the neat and composite systems have the same ordering kinetics (on the order of minutes) and produce a polycrystalline cubic phase. However, the differences are in the details of the OOT. Firstly, the added proteins can change the unit cell structure and alignment of the cylindrical phase, which inherently changes the OOT. In the neat systems, the OOT occurs via an epitaxial transition between BCC or FCC and HEX. Depending on the protein added, the OOT occurs between a cubic phase and a disrupted cylindrical phase, SQR, or HEX. Interestingly, in all of these cases, the OOT occurs via an epitaxial transition regardless of the structure and alignment of the cylindrical phase (Figure 6.5). The added protein affects the timescale of the OOT by increasing the transition time from 20 minutes to 30 minutes.

In the neat system, the OOT forms a partially aligned FCC or BCC oriented with the (110) plane parallel to the velocity vector. In the polymerparticle composite, the added proteins act as obstacles that the spherical micelles must arrange around. The added BSA has a greater effect on the polycrystallinity than the smaller protein lysozyme. Specifically, the added BSA increases the polycrystallinity of the formed cubic phase, making it more difficult to absolutely determine the orientation of the unit cell. However, the scattering from the neat and composite systems have similar symmetry, which suggests the added protein does not change the relative orientation of the cubic phase. It is also noted that added protein affects the shear alignment and flow mechanism of the soft solid, but this will not be commented on further since it has been discussed in Chapter 4.

As far as we are aware, this is the first time a direct transition from a square packed cylindrical phase to a cubic phase has been reported. Comparison of the SQR to FCC (Figure 6.5) and the HEX to FCC transition (for the neat P123 system) shows their scattering patterns undergo the same temporal evolution and exhibit similar symmetry. Based on these similarities, we propose the SQR to

FCC transition occurs by the same pathway as the transition from HEX to FCC with the cylindrical axis parallel to the (110) plane of the FCC crystal.

### **6.5 Conclusions**

The structural transitions in block copolymer soft solids are impacted by the formulation of the system. The soft solids are composed of spherical micelles arranged in a FCC or BCC cubic crystal, via temperature-induced structural transitions from a disordered liquid through the ODT or from aligned hexagonally close packed cylindrical micelles through the OOT. Hydrophilic nanoparticulate material (globular proteins BSA and lysozyme) is added to the solvent swollen interstices of the block copolymer soft solid. In comparison to the system without protein, the added protein impacts the OOT and not the ODT. Specifically, the added protein impacts the structure and alignment of the cylindrical phase, ordering kinetics, and polycrystallinity of the formed cubic phase. The added BSA changes the OOT transition in both block copolymer systems; in the P123 system OOT is between square packed cylindrical micelles and FCC while in the P103 system the OOT is between a disrupted cylindrical phase and BCC. The added protein increases transition time to 30 minutes. Regardless of the structure of the cylindrical phase, the OOT occurs via an epitaxial transition and produces a partially aligned cubic phase. The added protein increases the polycrystallinity of the formed cubic phase, but the orientation is the same as in the neat systems. The shear aligned structure and flow mechanism of these composite systems are insensitive to structural history. Overall, this work demonstrates that added proteins affect the kinetics and structural transitions of soft solids and establishes

the need to understand the impact of formulation on the structural behavior of these systems.

# 6.6 References

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#### **Chapter 7 Particle Stability in Concentrated Polymer Solutions**

This chapter focuses on controlling the spatial organization and aggregation of particles through manipulation of colloidal forces. The colloidal interactions that will be examined are steric, electrostatic, and depletion interactions. Control of the spatial distribution and aggregation of particles is vital for the development of new composite materials and applications.<sup>1–3</sup>

### 7.1 Introduction

Previous work has described a successful method for templating particles in interstitial spaces of block copolymer soft solids.<sup>4,5</sup> To achieve this templating, the implemented colloids form a stable dispersion in water such that the particles are stable enough to transition through the ODT without aggregating. The colloids chosen are electrostatically stabilized silica and globular proteins such as lysozyme and BSA that are used at a pH away from their isoelectric point (pI<sub>silica</sub>  $= \sim 2$ , pI<sub>BSA</sub> = 4.7-4.9, pI<sub>LYS</sub> = 11.35).<sup>6-8</sup> The silica particles and lysozyme remain stable in both the liquid and soft solid phases. However, the BSA aggregates at low temperatures in the liquid phase and re-disperses in the soft solid near room temperature.<sup>9,10</sup> The studies with BSA give the first indication that colloids unstable in liquid phase can be re-dispersed or templated in the soft solid. These results then beg the question; what will happen to the particles if the repulsive interactions are screened. Furthermore, will these soft solids still be able to template nanoparticles that are no longer stable in solution?

This chapter aims to answer these questions by determining the importance of colloidal interactions on the particle stability in these polymer systems. Figure 7.1 summarizes the experiments conducted, using particles with a relatively constant radius (a). Also, it shows a hypothetical phase boundary for this re-dispersion. In this chapter, sterically or electrostatically stabilized particles are added to concentrated polymer solutions to examine key colloidal interactions such as steric, electrostatic, and depletion interactions on particle stability. Section 7.2 determines the importance of repulsive steric interactions on the ability to spatially organize gold nanoparticles in the soft solid, where the degree of steric stabilization is controlled by the thickness of the adsorbed polymer layer ( $\delta$ ). Section 7.3 determines the impact of electrostatic stabilization on the stability of silica particles in these polymer solutions. The electrostatic stabilization is dependent on the Debye length ( $\kappa^{-1}$ ), which is screened by increasing the ionic strength. In both sections, depletion interactions are varied as the polymer solution structurally transitions from a disordered liquid to a soft solid.



← Inc. electrostatic stabilization

Figure 7.1: Example of the qualitative phase diagram that will be investigated from the experiments in Chapter 7.
The findings of this work provides additional design parameters required for successful templating of particles in the soft solids, and highlights the importance of using the structural transition in the polymer template to control the flocculation of particles.

# 7.2 Impact of steric stabilization on stability of gold particles

One objective of this work is to determine the impact of an order-disorder structural transition on the colloidal interactions between particles. The second objective is to determine the importance of steric stabilization on the ability to spatially organize particles in the soft solid. The polymer template is made from a concentrated polymer solution (25wt% Pluronic<sup>®</sup> F127 [PEO<sub>106</sub>-PPO<sub>70</sub>-PEO<sub>106</sub>] in water) that goes through a thermoreversible structural transition from a disordered liquid to a soft solid made of close packed spherical micelles.<sup>4,11,12</sup> The specific particles used in this work are synthesized gold nanoparticles functionalized with carboxyl-terminated thiols of varying chain length or mercaptosuccinic acid. The particles are sterically and electrostatically stabilized; the particles have the same degree of steric stabilization but varying amounts of steric stabilization. UV-Visible spectrophotometry is used to monitor the stability of the gold particles as the polymer matrix transitions between a soft solid and a disordered liquid. Small angle x-ray scattering (SAXS) is used to determine the separation distance and arrangement of particles in the soft solid.

# 7.2.1 Materials and Methods

Gold(III) chloride trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O), sodium borohydride (NaBH<sub>4</sub>), tetraoctylammonium bromide (TOAB), 6-mercaptohexanoic acid (MHA), 11-mercaptoundecanoic acid (MUA), and mercaptosuccinic acid (MSA) are purchased from Sigma Aldrich (St. Louis, MO). The 3-mercaptopropionic acid (MPA) is purchased from Tokyo Chemical Industry Co. (Tokyo, Japan), 4-(N,N-dimethylamino)pyridine (DMAP) is purchased from Oakwood Chemical (West Columbia, SC), and Polyethylene glycol MW 6000 (PEG6000) is purchased from Alfa Aesar (Haverhill, MA). All materials are used as received without further purification.

Colloidal gold is synthesized using a two-phase liquid-liquid system described by Brust et al.<sup>13</sup> An aqueous solution of gold(III) chloride trihydrate (0.025M, 10mL) is vigorously mixed with a solution of TOAB in toluene (0.05M, 25mL). Once the AuCl<sub>4</sub><sup>-</sup> ions are transferred into the organic phase, the aqueous phase is separated and removed. The AuCl<sub>4</sub><sup>-</sup> is reduced by dropwise adding an aqueous solution of sodium borohydride (0.4M, 10mL). This is followed by 6 hours continuous mixing, after which the organic phase is separated and removed. The particles are spontaneously phase transferred from the organic to the aqueous phase by using DMAP.<sup>14,15</sup> For the phase transfer, 2mL of a 0.1M aqueous DMAP solution is added to the organic phase followed by 100µL of a 0.3M DMAP solution thirty minutes later. Once the particles transfer to the aqueous phase (roughly 2hrs), the organic phase is remove and discarded. The gold particles are then functionalized with a carboxyl terminated thiol or MSA (Figure 7.2) which

replaces the DMAP and reverses the charge of the particles.<sup>16</sup> A thiol solution (in water or ethanol) is added to the solution of Au\_DMAP nanoparticles. The mixture is allowed to stand overnight for the ligand exchange to complete. The particles are stored as a stock solution of gold sol at room temperature.



mercaptoundecanoic acid (MUA)



mercaptosuccinic acid (MSA)

Figure 7.2: Carboxyl terminated thiols used as capping ligands for the synthesized gold particles.

Concentrated stock solutions of 35wt% F127 and 50wt% PEG6000 are prepared by dissolving the polymer in de-ionized water (18 M $\Omega$ ). Preparation of the stock solution requires the samples to be refrigerated up to seven days.

The polymer-particle samples are prepared by initially mixing the particle stock solution with the polymer stock solution, followed by vigorous mixing. The addition of the Pluronic<sup>®</sup> stock solution is done at low temperatures where the solution is a viscous liquid. The sample is a dilute polymer-particle solution of roughly 1.5wt% gold nanoparticles and 10wt% polymer. The samples are

dehydrated in a vacuum oven until a final concentration of 3wt% gold particles in 25wt% F127 (or 18.2wt% PEG6000) is achieved. The particle concentration is reported as a weight fraction of the total sample while the polymer concentration is reported as the weight fraction in the polymer-water solution.

UV-Visible spectroscopy is carried out using a Varian Cary 300 Scan UV-Visible Spectrophotometer (Agilent Technologies, Santa Clara, CA) in the visible range (350-800nm). The samples are loaded into quartz cuvettes with path lengths of 0.01mm or 0.1mm. An extinction spectra is measured in the visible range (350-800nm). Since the scattering cross-section is proportional to the square of the particle volume and the absorbance cross-section is proportional to the particle volume, the absorbance contribution is expected to dominate.<sup>17</sup> Thus the absorbance and extinction are assumed to be equal and scattering is neglected. For the gold sol, the absorbance at the characteristic peak is used with Beer-Lambert's law to estimate the concentration of particles in the stock solution. The molar extinction coefficient is estimated using the relation determined by Navarro and Werts<sup>18</sup> by assuming a particle diameter of 5nm.

SAXS is used to determine the size of the particle core and the spatial organization of gold particles in the soft solid. Samples are loaded at room temperature and thermally equilibrated at the desired temperature for 20 minutes before collecting scattering. The size of the gold core is determined by fitting the scattering intensity from the gold sol with a bimodal Schulz Spheres equation using Igor macros developed at NIST.<sup>19</sup> The particle size with the greatest number population (by at least an order of magnitude) is reported in Table 7.1.

The hydrodynamic diameter and zeta potential of particles are measured with a Malvern Zetasizer Nano ZS (United Kingdom) which uses a laser with a wavelength of 633nm. A folded capillary DTS 1060 cell is used for measuring the zeta potential, and a low volume polystyrene cuvette is used for the size measurements. The gold sol is diluted by at least a factor of 1000 prior to measurements.

The second virial coefficient of the particles is measured with a Brookhaven Instruments BI-200SM Laser Light Scattering Instrument (Holtsville, NY) using the Zimm plot software. The laser has a wavelength of 637nm, and the filter and pinhole are adjusted to achieve count rates of approximately 500kcps. The first sample is made by diluting the gold sol to a concentration  $\sim 10^{-2}$ mg/mL in an acid washed 20mL glass scintillation vial. Scattering for the sample is collected at least five angles at 10° increments. To this sample, aliquots of DI water are added to achieve different concentrations. After each dilution, a scattering measurement is taken. At least 5 concentrations are used, with the lowest concentration being  $\sim 3x10^{-3}$ mg/mL.

## 7.2.2 Results: Gold functionalized with carboxyl terminated thiols

Table 7.1 summarizes the properties of the synthesized gold nanoparticles. The gold nanoparticles are functionalized with carboxyl terminated thiols that have an alkane chain ranging from 2 to 10 carbons. In water, the functionalized gold particles have a zeta potential of -35mV showing the particles have the same degree of electrostatic stabilization. Additionally, the gold nanoparticles have a second virial coefficient  $A_2 = +1 \times 10^{-4} \text{mol} \cdot \text{mL/g}^2$ , measured using static light scattering. The positive value of  $A_2$  indicates the particle-particle interaction is repulsive, and the magnitude of  $A_2$  is consistent with values expected for 5nm hard spheres.<sup>20</sup> The gold core diameter is approximately the same for the different particles while the hydrodynamic diameter increases with ligand length.<sup>21</sup> The distinguishing factor between the particles is the thickness of the monolayer which provides the particles with varying degrees of steric stabilization.

Au_thiol	Ligand	#carbons in	Gold core	Zeta potential	$D_{h}(nm)$
		alkane chain	diameter (nm)	(mV)	
Au_MPA	MPA	2	$4.2 \pm 0.4$	-35	6.6
Au_MHA	MHA	5	$4.8\pm0.2$	-35	7.3
Au_MUA	MUA	10	$4.8 \pm 0.1$	-35	7.6

Table 7.1: Properties of synthesized gold nanoparticles.

UV-Vis spectrophotometry is used to monitor the stability of the gold sol. The unique absorbance spectra exhibited by colloidal gold is due to the surface plasmon resonance of the particle, which is dependent on the particle size and shape.<sup>22</sup> The spectra has a characteristic absorbance peak that is red-shifted when neighboring particles are in close proximity to one another.<sup>23,24</sup>

Figure 7.3 shows absorbance spectra for the gold sol at temperatures between 5°C and 70°C. The particle concentration ranges from 2wt% to 3wt% gold nanoparticles. The characteristic absorbance peak occurs at 519nm for Au\_MUA, 519nm for Au\_MHA, and 518nm for Au\_MPA. The wavelength of the absorbance peak is unaffected by temperature which indicates the gold sol is a stable dispersion in this temperature range. The absorbance data for 3wt% Au\_MHA in water is significant because it shows that the gold sol is stable at a higher particle concentration that is used in the soft solid experiments.



Figure 7.3: Absorbance spectra for the gold sol at several temperatures between  $5^{\circ}$ C and  $70^{\circ}$ C.

The following results examine the effect of the soft solid nanostructure on the stability and spatial organization of the gold nanoparticles. The soft solid is formed from a concentrated polymer solution (25wt% F127) that undergoes a thermoreversible structural transition.<sup>4,12</sup> Specifically, the polymer solution

transitions from a solution of unimers (5°C) to a micellar liquid (15°C) to a soft solid composed of water-swollen micelles packed into a cubic crystalline lattice (25°C-70°C).<sup>4,12</sup> The full details of the phase behavior and structure for F127 systems has been determined using small angle neutron scattering, visual observations, rheology, and DSC.<sup>4,12</sup> To the soft solid, 3wt% gold nanoparticles are added, which is equivalent to a particle loading of 1 gold particle per 6 octahedral interstitial spaces.

Figure 7.4 shows the absorbance spectra for 3wt% gold particles dispersed in a solution of 25wt% F127 in water. Absorbance is measured as the system is (a) heated from 25°C (soft solid) to 70°C (soft solid) and cooled to 25°C, and (b) cooled from 25°C (soft solid) to 15°C (micellar liquid) to 5°C (solution of unimers) and then reheated to 25°C (soft solid). In the soft solid, between 25°C and 70°C, the Au\_MUA particles have an absorbance peak at 523nm. As the system cools and transitions to a liquid, the absorbance peak remains at 523nm until 5°C, at which point the absorbance peak red-shifts to 531nm and the absorbance increases at higher wavelengths. After reheating the system to 25°C, the absorbance peak blue-shifts to 523nm.



Figure 7.4: Absorbance data for 3wt% gold particles in a solution of 25wt% F127 in water. The absorbance is measured as the system is (a) heated from  $25^{\circ}$ C to  $70^{\circ}$ C and cooled to  $25^{\circ}$ C, and (b) as the system is cooled from  $25^{\circ}$ C to  $5^{\circ}$ C and reheated to  $25^{\circ}$ C. The data collected during heating or cooling is represented by the solid lines while the data collected at  $25^{\circ}$ C after heating or cooling is represented by the dashed lines.

The gold particles functionalized with MHA and MPA display different absorbance spectra than the Au MUA particles in the soft solid. The Au MHA particles in the soft solid have an absorbance peak at 665nm at 25°C. Figure 7.4 (a) shows this absorbance peak is blue-shifted to 531nm as the system heats to  $70^{\circ}$ C. The absorbance peak shifts to 675nm as the temperature decreases from  $70^{\circ}$ C to  $25^{\circ}$ C. As the system transitions to a liquid, the absorbance peak red-shifts to 685nm at 15°C, before disappearing at 5°C. The absorbance peak reappears at 725nm once the system is reheated to 25°C. A similar trend in the absorbance data is displayed by the Au MPA particles. The Au MPA particles in the soft solid have an absorbance peak at 545nm at 25°C. In the soft solid, the absorbance peak is blue-shifted as the system is heated from 25°C to 45°C (540nm) to 70°C (531nm). However, the absorbance peak is shifts to 540nm after the system is cooled to 25°C. Cooling causes the absorbance peak to red-shift where it occurs at 555nm at 15°C and 572nm at 5°C. By heating to 25°C, the absorbance peak occurs at 560nm.

The fact that the absorbance peak for the Au\_MUA in the soft solid is at approximately the same wavelength as the gold sol (in Figure 7.3 (a)) suggests the gold particles are templated in the interstitial spaces of the soft solid. The slight different between the wavelengths could be due to differences in the refractive index of the medium.<sup>25</sup> As the system heats to 70°C, the absorbance peak remains at 523nm which shows that temperature does not affect the stability of the particles when dispersed in the soft solid. Structurally transitioning the system from a soft solid to a disordered liquid causes the absorbance peak to slightly red-

shift which means the gold particles are in closer proximity and possibly forming small clusters or aggregates in the liquid phase. The increased absorbance at higher wavelengths could be due to scattering from the polymer.

The gold particles functionalized with the shorter thiols, Au\_MHA and Au\_MPA, display similar behavior in the soft solid. For both Au\_MHA and Au\_MPA, the particles form a stable dispersion in water (Figure 7.3). However, the absorbance peak exhibits a red-shift when the particles are added to the soft solid. This red-shift indicates the soft solid is forcing the particles to come in close proximity and cluster. As the system heats to 70°C, the absorbance peak is blue-shifted to lower wavelengths which could be due to a decrease in the cluster size or an increase in the separation distance between the particles.<sup>23</sup> The transition from a soft solid to a liquid causes the absorbance peak to red-shift to greater wavelengths, signifying an increase in the cluster size. With respect to Au\_MHA, the clusters become so large that they no longer exhibit an absorbance peak. More importantly, the absorbance peak for all the gold particles at 25°C is approximately the same regardless of whether the system is heated or cooled suggesting the soft solid reverses clustering that occurs in the liquid phase.

SAXS is used to gather insight on the interactions between gold particles dispersed in the soft solid. Figure 7.5 compares the scattering intensity (I(q)) for the gold particles in water and in the soft solid (25wt% F127) at 25°C, 45°C, and 70°C. In the composite system consisting of gold particles in the soft solid, scattering comes from both polymer and particle components. However, the difference in the scattering length density (SLD) between gold and water

 $(\Delta SLD_{Au-H2O} = 1.2x10^{-4} \text{Å}^{-2})$  is several orders of magnitude greater than the difference between F127 and water ( $\Delta SLD_{F127-H2O} = 3.2x10^{-7} \text{Å}^{-2}$ ). Therefore, the gold particles dominate the scattering. Scattering from the soft solid (25wt% F127 at 25°C) is included to demonstrate how the scattering intensity from the composite is significantly greater than scattering from the polymer. Crystallography of the soft solid will not be discussed in this work, but SANS has determined the spherical micelles are packed into a face-centered cubic (FCC) crystal where the hard-sphere micelle diameter (D<sub>HS</sub>) is approximately 20nm.<sup>4</sup>

The I(q) for Au\_MUA in the soft solid (Figure 7.5 (a)) appears similar to the scattering from the Au\_MUA sol. However, scattering from the Au\_MHA and Au\_MPA in the soft solid have a peak at high q and an upturn at low q, relative to the scattering from the gold sol. From the scattering intensity in Figure 7.5 (a), the structure factor S(q) is calculated to gather information about the spatial organization of particles in the soft solid. This is done by normalizing I(q) by the form factor P(q) and a constant that accounts for differences in the particle concentrations. The P(q) describes the shape and size of the particle, and it is proportional to the measured scattering from the gold sol.



Figure 7.5: SAXS data for 3wt% gold particles dispersed in the soft solid (25wt% F127). (a) Scattering intensity I(q) for the gold particles in the soft solid at  $25^{\circ}$ C,  $45^{\circ}$ C, and  $70^{\circ}$ C. Scattering from the gold sol (open diamonds) and from the soft solid (open squares) are included for comparison. (b) Calculated structure factor S(q) for the gold particles in the soft solid.

Figure 7.5 (b) shows the S(q) for the gold particles in the soft solid between 25°C and 70°C. The S(q) for Au\_MUA has four low-intensity peaks at  $q/q^* = 1$ ,  $\sqrt{4/3}$ ,  $\sqrt{8/3}$ , and  $\sqrt{11/3}$  where q\* is the value of the primary peak. These q/q\* ratios indicate the gold particles are organized into a FCC crystal.<sup>26</sup> For the Au\_MHA and Au\_MPA particles in the soft solid, the S(q) has a peak at high q that shifts to lower q values with increasing temperature. For Au\_MHA, the peak occurs at 0.114Å<sup>-1</sup> at 25°C and shifts to 0.100Å<sup>-1</sup> at 70°C. For Au\_MPA, the peak occurs at 0.140Å<sup>-1</sup> and shifts to 0.134Å<sup>-1</sup> at 70°C.

From the value of q\*, the center-to-center distance  $(D_{C-C})$  between the particles is estimated. Because the Au\_MUA particles form a FCC crystal, their center-to-center distance  $(D_{C-C,FCC})$  is calculated using equation (7.1). For the Au-MHA and Au\_MPA particles, the crystal structure is unknown and  $D_{C-C}$  is calculated using equation (7.2).

$$D_{C-C,FCC} = \frac{\pi\sqrt{6}}{q^*}$$
(7.1)

$$D_{C-C} = \frac{2\pi}{q}$$
(7.2)

The  $D_{C-C,FCC}$  between Au\_MUA particles is approximately 20nm, or roughly the  $D_{HS}$  of the micelles. Since the Au\_MUA is organized in a FCC crystal with the same dimensions as the soft solid, the Au\_MUA must be spatially organized within the interstitial spaces of the soft solid and forming a FCC crystal intercalated with the FCC micelle structure.

Using equation (7.2), the  $D_{C-C}$  between Au\_MHA particles increases from 5.5nm at 25°C to 6.3nm at 70°C while the  $D_{C-C}$  between Au\_MPA particles

increases from 4.5nm at 25°C to 4.7nm at 70°C. This  $D_{C-C}$  is approximately equal to the particle diameter (core+ligand monolayer).<sup>21</sup> Therefore, the separation distance between the particles is negligible and the Au\_MHA and Au\_MPA particles cluster in the interstitial spaces of the soft solid. Additionally, the increase in the separation distance correlates to the red-shift displayed in the absorbance spectra (Figure 7.4). Since the particle-particle separation distance is temperature dependent, the added thermal energy appears to increase the thermal motion of the particles and their separation distance.

It important to note that if the 3wt% gold particles are homogeneously dispersed, the average  $D_{C-C}$  would be approximately 35nm. However, the SAXS data shows the soft solid decreases  $D_{C-C}$  to 20nm for Au\_MUA and clusters the Au\_MPA and Au\_MHA. Therefore, the soft solid nanostructure controls the separation distance between particles. Another interesting thing to note is that the particle loading is relatively low at 1 particle per 6 octahedral interstitial sites, yet the Au\_MUA particles form an intercalated FCC lattice with the soft solid, which requires a particle loading of 1 particle per interstitial site. This suggests there are particle rich and particle poor regions in the system, where the particle rich regions have a particle loading of 1 particle per interstitial site.

The gold particles are stored in the soft solid at room temperature for at least one week, after which the samples are diluted with water. The dilution changes the soft solid to a solution of unimers at 25°C.<sup>12</sup> Figure 7.6 shows absorbance spectra for the gold nanoparticle-soft solid samples after being diluted. After dilution, the absorbance peak occurs at 516nm for Au\_MPA,

518nm for Au\_MHA, and 521nm for Au\_MUA, which are approximately the same wavelength as the original gold sols (Figure 7.3). The absorbance peaks, along with dynamic light scattering (results not shown), show the original gold nanoparticles are recovered upon dilution. This is particularly significant because it demonstrates that gold particles can be stored as clusters in the soft solid and recovered at a later time.



Figure 7.6: Absorbance data for 3wt% gold nanoparticles stored in a soft solid (25wt% F127) after being diluted with water by a factor of 1000. The gold particles are stored in the soft solid at room temperature for at least 7 days prior to dilution. The Au\_MUA particles are stored in the soft solid for 2 years.

To isolate the effects from the PEO environment and the nanostructure, we examine the stability of the gold particles in a PEG6000 solution with the same PEO concentration as the soft solid (25wt% F127).<sup>27</sup> The system examined is 3wt% Au\_MHA in 18.2wt% PEG6000 in water. Similar to the soft solid experiments, this sample is stored at room temperature for 7 days before being diluted with water. Figure 7.7 (a) shows the absorbance spectra for 3wt%

Au\_MHA in water, and in 18.2wt% PEG6000 before and after dilution. The Au\_MHA sol has absorbance peak at 518nm and exhibits a red-wine color (Figure 7.7 (b)). In a solution of 18.2wt% PEG6000, the Au\_MHA particles do not have an absorbance peak in the visible region and form large, macroscopic clusters (Figure 7.7 (c)); this is similar to the particle aggregation in 25wt% F127 at 5°C (Figure 7.4 (b)). By diluting the system, the absorbance peak reappears at 519nm which is approximately the same wavelength as the original gold particles in water. Comparison of these results to the clustering behavior of Au\_MHA in the soft solid indicates the cluster size is controlled by the nanostructure of the soft solid and not by the PEO content.



(a) (b) (c) Figure 7.7: (a) Absorbance spectra for 3wt% gold particles functionalized with MHA dispersed in a solution of 18.2wt% PEG6000. Absorbance data for this system after being diluted with water by a factor of 1000 as well as the original gold sol are included for comparison. The sample is diluted after being stored at room temperature for 7 days. (b) Photograph of 3wt% Au\_MHA in water. (c) Photograph of 3wt% Au\_MHA in a solution of 18.2wt% PEG6000.

It is acknowledged that reversible clustering has been observed for MPA capped gold particles in water by varying the pH of the solution.<sup>28,29</sup> However, in this work, the added polymer does not significantly change the pH of the medium and the clustering observed is unlikely due to pH effects.

# 7.2.3 Results: Gold functionalized with mercaptosuccinic acid

Gold particles are synthesized using the method in Section 7.2.1 and functionalized with mercaptosuccinic acid (MSA). These particles have a core diameter of 5.5nm, a number averaged hydrodynamic diameter of 6.5nm, and zeta potential of -25mV. Figure 7.8 shows the absorbance spectra for 1.2wt% Au\_MSA in water between 5°C and 70°C. The absorbance peak is at 520nm between 5°C and 25°C. Heating above 25°C slightly broadens and red-shifts the absorbance peak, suggesting the Au\_MSA begins to aggregate above 25°C.



Figure 7.8: Absorbance spectra for 1.2wt% Au\_MSA in water at temperatures between 5°C and 70°C. Data from 5°C to 25°C are collected using a 0.1mm quartz cuvette while the 45°C and 70°C data use a 0.01mm quartz cuvette.

Figure 7.9 shows absorbance data for Au\_MSA in a solution of 25wt% F127 in water. Figure 7.9 (a) shows the absorbance data for Au\_MSA in the soft solid between 25°C and 70°C, and Figure 7.9 (b) shows the absorbance data as the soft solid (25°C) transitions to a liquid (5°C). In the soft solid, the absorbance peak is at 547nm between 25°C and 70°C. The absorbance peak decreases in magnitude and red-shifts to 576nm when the system is a liquid at 5°C. Reheating the system back to 25°C blue-shifts the absorbance to 560nm.



Figure 7.9: Absorbance data for 1.2wt% Au\_MSA in a solution of 25wt% F127 in water. The absorbance measured as the system is (a) heated from 25°C to 70°C and cooled back to 25°C, and (b) cooled from 25°C to 5°C and reheated to 25°C. Data collected during heating or cooling is represented by solid lines. Data collected after heating or cooling is represented by dashed lines.

The Au\_MSA nanoparticles behave similarly to the gold particles functionalized with MHA and MPA. When the particles are incorporated to the soft solid, the absorbance peak exhibits a red-shift signifying the soft solid is forcing the particles to cluster. In the soft solid, the stability of the particles is unaffected by temperature. However, the red-shift displayed upon transitioning from a soft solid to a liquid ( $5^{\circ}$ C) indicates the cluster size increases in the liquid state. Furthermore, reformation of the soft solid re-disperses some of the particles aggregated in the liquid phase.

SAXS is used in the same manner as previously describe to gather information about the spatial arrangement of Au\_MSA in the soft solid. Figure 7.10 (a) compares I(q) for Au\_MSA in water and in the soft solid at 25°C on day 0 and day 13. Day 0 is the day the gold-soft solid sample is prepared and the day the samples are loaded in the glass capillaries. The loaded capillaries are stored at room temperature until being re-examined 13 days later. Scattering for the gold sol is sensitive to time and exhibits a peak at high q after 13 days. Scattering from the Au\_MSA in the soft solid has a peak at high q and an upturn at low q with respect to scattering from the sol on day 0, but appears unaffected by time. Figure 7.10 (b) compares the S(q) for the gold particles in water and in the soft solid. The scattering from the gold sol on day 0 is used as the P(q) when calculating the S(q).



Figure 7.10: SAXS data for 1.2wt% Au\_MSA in water and in the soft solid (25wt% F127 at  $25^{\circ}$ C) collected on day 0 and day 13. Day 0 is the day the samples are loaded in the capillaries and also the day the gold-soft solid sample is prepared. The samples are left in the capillaries at room temperature and reexamined after 13 days. (a) Scattering intensity I(q) from the gold particles. (b) Calculated structure factor S(q) for the gold particles.

The scattering from the gold sol is time dependent suggesting the particles do not form a lasting stable dispersion in water. On day 0, the particles form a stable dispersion in water. Assuming the particles are homogenously dispersed, the center-center distance between the particles is approximately 55nm. On day 13, the S(q) of the gold sol has a sharp peak at  $0.102\text{Å}^{-1}$  that corresponds to a D<sub>C-C</sub> of 6.2nm (calculated using equation (7.2)). This distance is roughly equal to the diameter of the gold core and indicative of particle aggregation. Therefore, the SAXS data shows the gold sol destabilizes by day 13.

In the soft solid, the S(q) at day 0 and day 13 appear almost identical with a large upturn at low q and a peak at  $0.115\text{Å}^{-1}$ . The q position of the peak corresponds to a  $D_{C-C}$  of 5.5nm, equal to the diameter of the gold cores. Therefore, the distance between the particle surfaces is negligible, and the particles are clustering in the soft solid. Since there are no significant differences between the S(q) at day 0 and day 13, the degree of clustering of the particles remains unchanged with time. The gold particles are shown to aggregate in water with time, however the lack of change here suggests the soft solid is preventing further clustering of particles.

Overall, Au\_MSA particles form an unstable dispersion in water. When added to the soft solid, the particles form clusters in the interstitial spaces that increase in size as the system structurally transitions from a soft solid to a liquid. However, reformation of the soft solid is able to partially reverse the clustering. Furthermore, the particles can be stored as clusters in the soft solid for prolonged periods of time. Unlike the gold sol, the clustering in the soft solid is unaffected by time suggesting the soft solid is preventing further clustering of particles.

# 7.3 Impact of ionic strength on stability of silica particles

The objective of this section is to determine the impact of ionic strength on the stability of silica particles dispersed in concentrated polymer solutions. The polymer solution is 25wt% F127, 35wt% P123, or 33wt% P103 in water. All of polymer systems undergo a thermoreversible ODT from a disordered liquid at cold temperatures ( $\sim$ 5°C) to a soft solid with cubic structure at room temperature. The F127 and P123 soft solids have FCC crystal structure while the P103 soft solid has BCC crystal structure. By varying the block lengths, we are able to vary the structural features of the soft solid and determine its impact on the particle stability.

The silica particles are similar to the size of the interstitial space and will organize into the interstitial spaces between the micelles.<sup>4</sup> Charge screening is carried out by increasing the concentration of sodium chloride (NaCl) in the polymer-solvent matrix. UV-Visible spectrophotometry is used to monitor the particle aggregation as the polymer matrix transitions between a soft solid and a disordered liquid. Rheology is used to determine the impact of the aggregates on the thermal behavior of the polymer template.

### 7.3.1 Materials and Methods

The samples are prepared by initially diluting the particle suspension with water. To this particle dispersion, the necessary amount of concentrated polymer solution is added. The concentrated polymer stock solutions are 35wt% F127, 43wt% P123, and 43wt% P103 in de-ionized water (18 M $\Omega$ ). The addition of the Pluronic<sup>®</sup> stock solution is done at low temperatures where the solution is a viscous liquid (~5°C). The samples are gently mixed to prevent the formation of a particle-stabilized foam. Once the sample is well mixed, the necessary amount of an aqueous 1M or 2M NaCl solution is added, followed by gentle mixing. The samples are allowed to equilibrate in the refrigerator for up to five hours, after which they are subjected to spectroscopy and rheological experiments. The particle concentration is reported as a weight fraction of the total sample while the polymer and salt concentrations are reported as the weight fraction and molarity in the polymer-water solution, respectively.

UV-Visible spectroscopy is used to monitor the flocculation of the colloidal silica. In general, spectroscopy measures the transmission of light (T) through the sample. In the previous section, changes in the light transmission result from absorbance by the gold particle. Since colloidal silica is non-absorbing, diminished light transmission results from increased turbidity or scattered light caused by particle aggregation. The spectrophotometer measures the light transmission and coverts it to extinction, where increasing extinction corresponds to the onset of particle aggregation.

For these experiments, the extinction at 450nm is chosen for analysis. At this wavelength, the extinction is negligible for both the polymer solutions as well as the colloidal silica and any increase in extinction is a result of particle aggregation. Temperature is adjusted using a multi-block Peltier unit. The samples are loaded as a liquid into disposable polystyrene low-volume cuvettes with a 10mm pathlength and equilibrated in the refrigerator to remove bubbles that arose during loading. Two types of experiments are conducted. The first is a temperature sweep experiment which follows a specific temperature protocol. A measurement is made at several temperatures as the system is heated from 3°C to 25°C. At each desired temperature, the sample is thermally equilibrated for 20 minutes prior to the measurement. After heating to 25°C, the sample is cooled to 3°C and equilibrated for 30 minutes before taking a final measurement. The other experiment examines the impact of ionic strength on the aggregation of silica particles in the soft solids. After the samples are prepared, they are stored at room temperature for at least an hour before taking measurements at 25°C.

Rheometric temperature sweeps are used to determine the impact of particle aggregation on the thermal response of the polymer template. For samples containing salt and silica, the samples are loaded as a liquid immediately after the samples are prepared. For the samples that do not contain salt, the samples are stable for long periods of time and may be tested days after preparation. Samples are equilibrated at 3°C for 5 minutes to eliminate any loading effects. The magnitude of the complex modulus is measured as the system is heated and cooled between 3°C and 45°C at a rate of 1°C/min.

# 7.3.2 Results

The structure and phase behavior of the polymer solutions implemented have been thoroughly characterized in the previous chapters and well as in previously published work. The salt concentrations used in this work are relatively low and do not impact the structure, phase behavior, or mechanical response of the polymer.<sup>30-33</sup> Additionally, the salt concentrations used are well below the critical coagulation concentration for colloidal silica in water at pH~7.<sup>6</sup>

Figure 7.11 shows pictures of particle-polymer composites with varying amounts of NaCl immediately after being taking out of the refrigerator ( $\sim 5^{\circ}$ C) and at room temperature. The samples contain 3wt% silica with polymer-solvent matrix of (a) 25wt% F127, (b) 35wt% P123, or (c) 33wt% P103 in water. The photos are of the samples immediately after being taken out of the refrigerator  $\sim 5^{\circ}$ C (row 1), after being stored at room temperature as a soft solid for 1 day (row 2), and "melted" after being stored at room temperature for 5 days. The samples are liquid-like at  $\sim 5^{\circ}$ C and solid-like at room temperature.



Figure 7.11: Photographs of polymer-silica composite samples with varying NaCl concentration. The samples contain (a) 25wt% F127 with 3wt% silica, (b) 35wt% P123 with 3wt% silica, and (c) 33wt% P103 with 3wt% silica. After the adding the salt, the samples equilibrated in the refrigerator for 1hr, then left at room temperature for 5 days, and then melted by placing in the refrigerator for an hour. Row 1 shows photographs of the samples in the liquid phase (~5°C) one hour after adding NaCl, row 2 shows photographs of the samples after being stored as a soft solid (room temperature) for 1 day, and row 3 shows photographs of the samples after being melted on day 5.

For the polymer systems used in Figure 7.11, an increase the salt concentration results in an increase in turbidity. Upon closer examination, we observe many other interesting features. For 25wt% F127 with 3wt% silica in the liquid phase (Figure 7.11 (a) row 1), a sharp increase in turbidity occurs at 75mM

NaCl. This sharp transition persists as the polymer forms a soft solid and after the system is melted (Figure 7.11 (a) rows 2 and 3). This indicates the aggregation induced in the liquid phase persists through the ODT and is irreversible.

For the P123 and P103 samples in the liquid phase (Figure 7.11 (b) and (c), row 1), all of the samples containing salt observe some degree of turbidity. In the P123 system, the turbidity gradually increases with salt concentration while in the P103 system all samples that contain salt appear highly turbid. Upon formation of the soft solid (row 2), the turbidity appears to decrease. However, the turbidity increases when the samples are melted (row 3). This apparent reversibility in turbidity suggests the formation of the soft solid reverses aggregation prompted in the liquid phase, and the degree aggregation can be controlled through the structural transition of the polymer solution.

To highlight temperature dependence of turbidity, Figure 7.12 shows time lapse photos for 35wt% P123 with 3wt% silica and 25mM NaCl. The pictures are collected immediately after the sample is removed from the fridge (T ~  $3^{\circ}$ C) while it warms to room temperature. These photos clearly show a decrease in turbidity which signifies the re-dispersion of the aggregated silica. This reversible phenomena has been previously observed for the globular protein BSA in various Pluronic<sup>®</sup> systems.<sup>9,10</sup>



 $\sim$  3°C  $\longrightarrow$  Room temperature

Figure 7.12: Time lapse pictures of 35wt% P123 with 3wt% silica and 25mM NaCl as the sample transitions from a liquid (~3°C) to a soft solid at room temperature.

Spectrophotometry is used to quantify this temperature dependent phenomenon by measuring the extinction at 450nm at different temperatures during heating. For the following experiments, the samples chosen are ones that observed turbidity in the liquid phase. Figure 7.13 shows the extinction as the samples are heated from 3°C to 25°C through the ODT. Data for the composite samples without salt are included for comparison as diamond symbols to show that these samples are optically clear. The dashed bars represent the temperature where the ODT occurs. Extinction for the samples at 3°C after being heated to 25°C is included to show the reversibility of the turbidity. For 25wt% F127 with 3wt% silica and 80mM NaCl, the samples remain turbid in both the liquid and soft solid with an average extinction of 1.36. The extinction remains approximately the same after being melted from a soft solid to a liquid (open symbol).



Figure 7.13: Extinction of nanocomposite samples as the sample warms from  $3^{\circ}$ C to  $25^{\circ}$ C. Extinction for the sample after being cooled from  $25^{\circ}$ C to  $3^{\circ}$ C is shown by the open symbols. The dashed bars represent the temperature at which the system transition from a liquid to a soft solid.

For the P123 and P103 composite samples with salt (Figure 7.13), the extinction is greatest at low temperatures ( $\sim$ 3°C). The extinction decreases as the temperature approaches the T<sub>ODT</sub> and maintains relatively constant at temperatures above the T<sub>ODT</sub>. Melting the system at 3°C increases the extinction to roughly the same value measured prior to heating. The decrease in the extinction indicates the silica particles are re-dispersed in the soft solid, while the reversibility of the extinction indicates the structure of the polymer matrix controls the degree of aggregation. These trends agree with the observations made from the photos in Figure 7.11.

Figure 7.14 shows the magnitude of the complex modulus of these samples obtained from rheology. The modulus is measured as the samples are heated and cooled between 3°C and 45°C. Rheological data for the neat system (without silica and salt) is included for comparison as the closed circles and is measured during heating and cooling from 5°C to 45°C. The dashed vertical lines denote the temperature at which the soft solid forms ( $T_{ODT}$ ). The  $T_{ODT}$  has been previously defined as the temperature at which the storage modulus becomes greater than the loss modulus (G'>G''). For these experiments, the criterion has been modified to require that the sample observe solid-like behavior and no longer flow when the vial is tilted. The reason for this is that the F127 composite system with 80mM NaCl has a G'>G'' at 10°C, however, the sample readily flows at 10°C and does not demonstrate solid-like behavior until the temperature is greater than 15°C.



Figure 7.14: Magnitude of  $|G^*|$  as a function of temperature for the composite systems. Results are for samples containing 25wt% F127 with 3wt% silica and 0 or 80mM NaCl, 35wt% P123 with 3wt% silica and 0 or 25mM NaCl, and 33wt% P103 with 3wt% silica and 0 or 25mM NaCl. Data for the neat system (only polymer) is included for comparison as closed circles. Samples are heated at a rate of 1°C/min and probed with small amplitude oscillations (0.5%, 1rad/s). The vertical lines denote the T<sub>ODT</sub>. The neat F127 data is collected using 10Pa and 1rad/s between 5°C and 17°C, and 50Pa and 1rad/s between 17°C and 45°C.

For each system, the heating and cooling curves for the composite with and without salt have the same general trend as the neat system. At temperatures above the  $T_{ODT}$ , the added silica and salt does not significantly impact the modulus of the soft solid, indicating the mechanical behavior of the soft solid is insensitive to particle aggregates. This is particularly significant for the P123 and P103 systems because it suggests the aggregation does not impact the OOT of these soft solids.

Below the  $T_{ODT}$ , there are some differences between the moduli of the composites with and without salt. In the F127 composite system, the addition of salt increases the modulus at temperatures between 10°C and 16°C where the polymer forms a micellar fluid.<sup>12</sup> For the P103 composite system with salt, the modulus of the liquid decreases as the system approaches the ODT while the corresponding composite sample without salt has a constant modulus of ~10<sup>-1</sup>Pa in this same temperature range. For the P103 composite sample with salt, the inverse relationship between the modulus and temperature matches the temperature dependence of the extinction (Figure 7.13), and shows that the aggregation does affect the mechanics of the liquid phase.

It is important to reiterate that varying the block lengths of the polymer changes the structural features of the soft solid. Specifically, F127 and P123 form soft solids with FCC crystal structure while P103 forms a soft solid with BCC crystal structure.<sup>9,10,34</sup> Additionally, the P123 and P103 micelles have larger cores and thinner coronas than F127 micelles.<sup>27</sup> Since prior work shows these structural features are a key component to controlling particle diffusivity in the soft solid,

the last part of this section focuses on how the structural features can be used to control the aggregation of silica. Figure 7.15 shows the impact of the soft solid's structural features on the aggregation of silica particles. In the F127 composite, there is a rapid increase in the extinction between 70mM and 80mM NaCl while the P123 and P103 composites observe a gradual increase in extinction with increasing salt concentration. At relatively high salt concentrations (>70mM NaCl), the extinction of the F127 composite systems are at least double the extinction of the P123 and P103 composite systems. This suggests that the P123 and P103 soft solids are more effective at re-dispersing the silica particles.



Figure 7.15: Extinction of composite samples at 25°C (soft solid) as a function of NaCl concentration. Results are for samples containing 25wt% F127, 35wt% P123, or 33wt% P103 with 3wt% silica and varying concentrations of NaCl.

In addition to the block lengths, the polymer concentration is another knob that can be used to tune the structural features of the soft solid. In the case of P123, decreasing the polymer concentration from 35wt% to 30wt% P123 increases the diffusivity of 7nm particles through the soft solid by almost an order of magnitude and shifts the system closer to the critical concentration at which the system transitions to a liquid at ambient conditions.<sup>27</sup> Figure 7.16 shows photographs comparing the composite samples containing 30wt% or 35wt% P123 with 3wt% silica and 0mM or 25mM NaCl. The photos are taken after the samples are stored at room temperature for two weeks as soft solids. Text is placed behind to highlight the differences in the haziness of the samples. Comparison of the photos shows the samples with 30wt% P123 are hazy while the samples with 35wt% P123 are transparent enough to read the text behind the photo; this difference is an indication that the aggregation behavior in the soft solid can be tuned by polymer concentration.

### 0mM NaCl

### 25mM NaCl



(L) 30wt% P123 with 3wt% silica(R) 35wt% P123 with 3wt% silica.

Figure 7.16: Photographs of 30wt% or 35wt% P123 with 3wt% silica and varying concentrations of NaCl. These photographs are taken after storing the samples at room temperature for two weeks.

## 7.4 Discussion

In this chapter, gold and silica nanoparticles are dispersed in polymer solutions. Figure 7.17 simplistically summarizes the different types of flocculation observed. The results include those presented in this work as well as in previously published work.<sup>9,10</sup> Particles that are stable in both the liquid and soft solid are represented by closed symbols, particles that are not stable in either phase are represented by open symbols, and particles that aggregate in the liquid and re-disperse in the soft solid are represented by the half-filled symbols. The gold symbols represent data from the gold experiments (Section 7.2), and purple symbols represent data from the silica experiments (Section 7.3). Black symbols indicate that these observations hold true for these specific particles in all polymer systems. For the silica experiments, particles are considered re-dispersed if the extinction is within five times the extinction of the composite without salt. The data for silica, BSA, and lysozyme have  $\delta/a\sim 0$ , but the results are shifted vertically for clarity.



Figure 7.17: Phase diagram summarizing the aggregation behavior of nanoparticulate material in the polymer matrix. Results from the gold experiments (Section 7.2) are gold circles, results from the silica experiments (Section 7.3) are purple symbols, and findings that hold true for all polymer systems used are black symbols. Filled symbols indicate the particles are stable in the liquid and soft solid, half-filled symbols indicate the particles re-disperse, and open symbols indicate the particles are unstable in both phases. Results for the silica and protein systems have  $\delta/a \sim 0$  and are shifted vertically for clarity.

In the phase diagram, there is no clear phase boundary that delineates irreversible aggregation and the re-dispersion effect. At small  $\kappa a \ll 1$  (no salt), silica particles are electrostatically stabilized while the gold particles are sterically and electrostatically stabilized. Both types of particles are similar in size with approximately the same zeta potential. However, these particles observe vastly different behavior; silica particles are stable in both the liquid and soft solid while the gold particles can form clusters, indicating the electrostatic stabilization is not adequate to disperse gold particles in these concentrated polymer systems. Rather, the clustering of the gold particles depends on the thickness of the steric layer. For gold particles that cluster, the soft solid can reduce the size of the cluster but not fully re-disperse the particles. The difference in the flocculation behavior is due to the gold having a greater effective Hamaker constant (A<sub>eff</sub>) and van der Waals attractions than silica and BSA (Table 7.2).<sup>34–36</sup> To demonstrate this, Figure 7.18 shows an estimated interaction potential (van der Waals + electrostatic) for the different particles in DI water.

		Particle radius, a	
Material	$A_{eff}(x10^{20}J)^{34-36}$	(nm)	ψ (mV)
Gold	30	2.5	-35
Silica	0.48	3.5	-40
BSA	0.75	3.5	-16.5

Table 7.2: Parameters used to estimate van der Waals and electrostatic interaction potentials.


Separation distance between surfaces of particles (nm) Figure 7.18: Sum of van der Waals and electrostatic interaction potentials for the different particles used as a function of particle separation distance.

The potentials are calculated using equations (7.3) and (7.4), where r is the center-center particle separation distance and h is the separation distance between two particle surfaces. Table 7.2 shows the parameters input into these equations. Assumptions implemented are that surface potential  $\psi$  is equal to the measured zeta potentials,  $\kappa^{-1} = 3 \times 10^{-8}$ m, and the temperature is 25°C.<sup>35</sup>

$$\frac{\Phi_{\rm VDW}}{k_{\rm B}T} = -\frac{A_{\rm eff}}{6k_{\rm B}T} \left( \frac{2a^2}{r^2 - 4a^2} + \frac{2a^2}{r^2} + \ln\frac{r^2 - 4a^2}{r^2} \right)$$
(7.3)

$$\frac{\Phi_{\rm el}}{k_{\rm B}T} = \frac{2\pi\varepsilon_{\rm o}\varepsilon_{\rm r}a\psi^2\ln(1+e^{-\kappa h})}{k_{\rm B}T}$$
(7.4)

The steric interaction potential for the gold particles in not included (Figure 7.18), however, the potential shown is comparable to the VDW+electrostatic+steric interaction potential for Au\_MSA. These estimated potentials highlight the fact that gold particles have a deeper and broader potential

well than silica and BSA and the importance of considering the material properties of the particles when designing a system.

At  $\kappa a > 1$ , aggregation of silica particles (purple symbols in Figure 7.17) is tuned by the ionic strength and structural features of the polymer matrix. As a result, three types of flocculation are observed: a stable dispersion in the liquid and soft solid, aggregation in the liquid and soft solid, and the re-dispersion previously observed for BSA.<sup>9</sup> For the particle and salt concentrations implemented, re-dispersion is only observed in a solution of 35wt% P123, signifying the stability of particles is highly dependent on the structural properties of the system.

In the literature, re-dispersion is proposed to be result of the polymer structural transition shifting the depletion attraction from the colloid limit to the protein limit.<sup>9,38,39</sup> The colloidal limit is where the radius of the particle (a) is greater than the characteristic size of the polymer such as the radius of gyration ( $R_{poly}$ ), while the opposite relation defines the protein limit (a< $R_{poly}$ ).<sup>38,39</sup> The protein limit is more stable than the colloidal limit based on the scaling of the depletion attraction.<sup>38,39</sup> In these thermoresponsive systems, the liquid phase (~5°C) is described by the colloid limit where the particles are larger than the polymer which is assumed to exist as unimers. The strong depletion attraction in the colloid limit is able to induce aggregation of BSA and gold particles with less steric stabilization. Self-assembly of the micelles shifts the system to the protein limit, where the polymers are the micelles that have a radius (~10nm) greater than or equal to the size of the particle.

For systems that remain aggregated in the soft solid, the size specific aggregate is reminiscent of an ideal cluster fluid. In an ideal cluster fluid, the cluster size is controlled by the repulsive barrier of an individual particle.<sup>40</sup> However, our system is more complex in the fact that the particles are confined to the PEO-rich environment by the steric repulsions exerted by the close packed micelles. Since the gold experiments with PEG6000 (Figure 7.7) prove the cluster size is not controlled by the PEO environment but rather the ordered nanostructure, it is hypothesized that the cluster size is limited by the entropy gained upon the formation of the soft solid. The crystalline order of the soft solid is entropically favored to increase the translational energy of each micelle.<sup>9</sup> In the presence of particles aggregates, the micelles must reorganize around the clusters which results in an entropic penalty due to a decrease in the translational energy. Therefore, the aggregate size is believed to be balanced by the entropic penalty incurred by the soft solid.

Overall, this chapter shows the ability to predict the stability of the particles is complex; it depends on parameters such as the material properties and surface functionality of the particle, block length of the polymer, and structural features of the polymer matrix. Depending on the material properties of the particle, the templating ability may depend on the degree of steric stabilization more than the electrostatic stabilization. Manipulation of the ionic strength as well as the block length of the polymer will enable the particles to re-disperse in the soft solid, and it demonstrates the feasibility of templating particles in environments with higher ionic strengths. Finally, the flocculation of the particles

responds to the reversible structural features of the polymer matrix. These findings emphasize the need to further study the influence of colloidal interactions in these composite systems to identify design parameters important for templating and highlight the ability to use these thermoresponsive systems for applications that require tunable aggregation.

## 7.5 Summary

This chapter demonstrates that the impact of colloidal interactions on the flocculation of particles dispersed in soft solids. Two types of hydrophilic particles are added: sterically and electrostatically stabilized gold particles and electrostatically stabilized silica particles. By varying the length of the stabilizing ligands and the ionic strength of the polymer-solvent matrix, we are able to examine the importance of steric and electrostatic stabilization on particle templating. The structural features of the polymer matrix are manipulated through temperature, concentration, and polymer block length to change the depletion attractions.

Particulate material can observe three types of flocculation: stability in the liquid and soft solid, aggregation in the liquid and soft solid, or re-dispersion, where the particles are aggregate in the liquid phase but disperse in the soft solid. Particle stability is highly dependent on the material properties of the particles and structural features of the polymer template. Of the systems studied, gold particles are either stable or unstable in both phases depending on the degree of steric stabilization, and for silica particles, the ionic strength and polymer block lengths can be tuned to access any of the three types of flocculation. In general, these

results show the aggregation in these systems is complicated and provides additional design parameters for successful templating of particles.

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# **Chapter 8 Conclusions**

The soft solids of interest, formed from concentrated polymer solutions, can undergo order-order structural transitions, be aligned by shear fields, and template hydrophilic nanoparticulate material in the solvent-rich interstitial spaces. However, an understanding of the impact of processing conditions and formulation on block copolymer soft solids is crucial for developing applications and effective processing of these materials. This work has three main contributions to this understanding: 1) identification of how processing conditions, specifically applied flow and temperature, impact the structural properties and timescales of the soft solid, 2) documentation of how added nanoparticles impact the processing of soft solids, and 3) demonstration of how manipulating the structural features and the formulation (such as particle type and added salt) influence the stability of particles in the polymer matrix.

#### 8.1 Impact of processing conditions on soft solids

The effect of processing conditions and formulation are described in terms of the structural parameters and flow mechanism of the soft solid. The P123 and P103 soft solids observe temperature-induced structural transitions from a disordered liquid, to a cubic structured soft solid, to a cylindrical structured soft solid. The thermoreversible phase behavior permits the cubic phase to be formed through different structural histories; the cubic phase forms via a disordered liquid through the ODT or from an aligned cylindrical phase through the OOT.

The cylindrical phases of the P123 and P103 systems have the same HEX structure that shear aligns into a persistent single crystal with the cylindrical

micelles parallel to the shear direction. The modulus of the HEX phase decreases after the cessation of shear, suggesting the polycrystalline cylindrical phase is quasi-stable. Radial scattering patterns show the applied shear induces undulations or bends in the P123 cylindrical micelles but not for the P103 micelles, suggesting that the P123 micelles have a greater degree of flexibility.

Although P123 and P103 have similar block lengths, their cubic phases have different unit cell structures, possibly due to residual polymeric impurities in the system. The P123 soft solid has a FCC structure while the P103 soft solid has a BCC structure. For both P123 and P103 cubic phases, the morphology of the micelle, unit cell structure, and modulus are invariant to changes in structural history. However, structural history greatly impacts the ordering kinetics and polycrystallinity of the cubic phase. The ODT requires minutes to form a polycrystalline cubic phase while the OOT requires tens of minutes to produce a partially ordered cubic phase with the (110) plane parallel to the walls of the cell. The source of this partial alignment is an epitaxial transition as the cubic phase forms from the pre-aligned cylindrical phase. Based on the scattering projections gathered, it is postulated that the cylindrical axis is coincident with the [112] direction of the BCC and FCC crystal, however a third projection is necessary for verification. Application of high amplitude oscillations will macroscopically align the micellar structure into a persistent near single crystal without shear banding the system. For both systems, the (111) plane of the cubic unit cell is aligned parallel to the velocity direction. In the P123 cubic phase, the applied shear decorrelates the close packed layers and changes the FCC stacking to a RCP

stacking. The P103 cubic phase remains BCC after the cessation of shear, however, the cubic phase formed through the OOT is more polycrystalline which indicates it is more difficult to align than the cubic phase formed through the ODT.

#### **8.2 Impact of formulation on soft solids**

To characterize the impact of formulation on the structural parameters of the soft solid, the globular protein BSA, similar in size to the interstitial space, is added to both P123 and P103 systems. The cylindrical phases of the P123 and P103 systems have similar dimensions yet the added BSA affects the systems differently. The added BSA changes the unit cell structure of the P123 cylindrical phase from HEX to SQR while persistently aligning and disrupting the packing of the P103 micelles. This difference in behavior suggests there are other factors of importance such as the rigidity of the cylinders or interactions between the polymer and protein.

For the soft solid in the cubic phase, the added BSA does not appear to affect the ODT but it does impact the OOT. Because the added BSA changes unit cell structure or alignment of the cylindrical phase, the OOT is characteristically different. More importantly, the OOT occurs via an epitaxial transition regardless of these differences, which requires approximately 30 minutes and produces a cubic phase that is more polycrystalline than in the neat system. After the cessation of shear, P123 and P103 cubic phases display transient structural and mechanical behavior that are relatively insensitive to structural history. In the P123 system with BSA, the cubic phase initially aligns into a twinned FCC crystal that slowly reorients over 90 minutes. The P103 cubic phase with BSA displays a rapid transition on the timescale of minutes that is likely due to a shear-induced phase transition that reverts after the cessation of shear. For these composite systems, it is more difficult to shear-align the micellar crystals into a single crystal and the resulting structure is more polycrystalline.

For the P103 system, experiments are also conducted investigating the impact of the smaller protein lysozyme on the structural properties of the soft solid. The rheological experiments and SANS show the added lysozyme does not impact the structure, mechanics, or alignment of the cylindrical phase. The added lysozyme also does not affect the ordering kinetics, structural properties, or shear alignment of the cubic phase.

#### 8.3 Control of particle stability

The flocculation of particles in the polymer matrix depends on the formulation and structural properties of the system. Formulation is changed by varying the nanoparticle material (silica versus gold), particle surface chemistry, and the addition of salt. The structural properties of the system, such as whether the system is a liquid or a soft solid, are adjusted by concentration, temperature, and length of the polymer blocks. Combined, these variables control the van der Waals, electrostatic, steric, and depletion interactions. As a result, three types of flocculation behavior are be observed: a stable dispersion in the liquid and templating in the soft solid, aggregation in the liquid and templating occurs in the soft solid.

Nanoparticles made from materials with varying Hamaker constants display different flocculation in the polymer matrix. The particles used have approximately the same degree of electrostatic stabilization, but the gold particles have stronger van der Waals attraction due to its Hamaker constant that is two orders of magnitude greater. This variation in attractive interactions allows the silica particles to be stable in both liquid and soft solid phases while gold particles are either stable or aggregated in both phases. The templating of gold nanoparticles is controlled by the length of the stabilizing ligand or degree of steric stabilization, and for gold particles that aggregate, the aggregate size is controlled by the ODT. Further studies with purely sterically stabilized nanoparticles are required to decouple steric and electrostatic effects.

We also investigated the impact of the soft solid nanostructure and electrostatic stabilization on the stability of silica nanoparticles. The electrostatic stabilization is screened by increasing the ionic strength (concentration of NaCl) of the polymer matrix. As previously mentioned, without salt, silica particles are stable in the liquid and soft solid phases of the three polymer systems studied. Screening the charge and controlling the polymer block lengths allows access to the three different types of flocculation behavior.

## 8.4 Research Impact

This research impacts the block copolymer solution community as well as informs of new potential applications for these soft solids. With respect to block copolymer solutions, the findings presented here provide new insight on the pathway and timescales associated with the structural transitions. Additionally, this thesis contributes to the understanding of how processing conditions impact soft solids, and more importantly, lays the foundation for understanding how soft solids respond to changes in formulation. Utilizing this information will improve the processing of these materials.

This research identifies additional design features for particle templating as well as for the control of particle flocculation behavior. The findings also show that, in the case of the gold particles, soft solids are able to store the particles for years, which is of particular interest to the colloids and pharmaceutical industries for long-term storage applications. Furthermore, this thesis demonstrates the unique ability of using the ODT and soft solid features to control the aggregation behavior and aggregate size. As demonstrated by the gold and silica particles, the controlled aggregation allows for the production of materials with specific optical properties. This opens up new avenues of applications for these composite systems such as sensing devices and novel materials.<sup>1,2</sup>

## 8.5 Future Work

The findings in this work are centered on the use of spherical nanoparticles, and the work in Chapter 7 is an initial effort to understand the impact of colloidal interactions on particle stability. There are several directions that future work on soft solids could take to extend this work.

One avenue would be to continue the colloidal perspective by further mapping out the phase space for the different flocculation behavior. Suggested experiments include using purely sterically stabilized nanoparticles to isolate the design requirements for these types of particles. This could be achieved by using the synthesized gold nanoparticles and adding salt to screen the electrostatics. To solely study the impact of van der Waals interactions, electrostatically stabilized nanoparticles that do not interact with the polymer and that have with roughly the same charge and size but varying Hamaker constants could be used. Therefore, any differences in aggregation would be a result of the particle material. Using the same electrostatically stabilized particles, increasing the ionic strength of the system will provide the additional information about the effect of electrostatic interactions. Furthermore, this work can be expanded to examine the impact of the OOT on particle stability. Prior work has shown the particles will form linear arrays in the cylindrical phase, and it would be interesting to know if this particle arrangement could also change the aggregate size or behavior.<sup>3</sup> The same experimental techniques used in this work could be used for this study.

Another avenue would be to demonstrate the feasibility of soft solids to template non-spherical particles. Possibilities include rod-like, cylindrical, cubic or disc-like inorganic and organic nanoparticles. It would be of interest to determine the influence of particle shape on the phase behavior and robustness of the soft solid. Once this has been established, it would be of great interest to understand how these different shapes impact the structural features and flow mechanism of the soft solid. The findings of this work would influence applications requiring non-spherical particles.

# 8.6 References

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#### Appendix A Persistently aligned rod-like micelles

Wormy micellar systems exhibit unique structure-property relationships that have been exploited for applications such as oil recovery and personal care products.<sup>1–4</sup> Depending on the concentration, these systems vary from an isotropic solution of entangled micelles to birefringent nematic or hexagonally packed phases (HEX).<sup>5–7</sup> At rest, the micelles are unaligned, or in the case of the hexagonal phase, the system is polycrystalline, composed of ordered domains of close packed micelles that are randomly oriented and separated by defects such as grain boundaries.<sup>8–11</sup> The mechanical and structural properties of wormy or rod-like micelle systems are highly dependent on processing and can exhibit a wide variety of flow-induced behavior including shear thickening, shear banding, flow alignment, and shear induced structures.<sup>8–22</sup>

Rheology has long been used, in conjunction with other techniques such as birefringence and scattering, to examine the structure-property relationship. A Couette cell or cone and plate with very low angles are the geometries most commonly used.<sup>4</sup> Successful applications of these techniques to elucidate information about the structure-property relationship are largely owing to the fact macroscopic alignment is only induced by applied flow fields and not by the chosen geometry.

Despite the findings above, one of the conclusions in Chapter 4 is that the added protein can generate a persistently aligned HEX structure that cannot be changed through applied shear. All prior work has shown these soft solids are initially polycrystalline but can be macroscopically aligned through application of steady or oscillatory shear.<sup>13,23–25</sup> To our knowledge, this is the first time a prealigned or persistently aligned cylindrical structure has been observed. The results presented here, provide more information about the consistency of the alignment prior to shear, the persistency of the alignment after shear, and the possible influence of the curvature of the Couette cell on the alignment.

#### A.1 Methods

The P123 and P103 neat and composite systems discussed in this chapter have the same formulation as those in Chapter 4. Due to the native hydrophilicity of the globular protein, the protein sequesters to the solvent-rich interstices between the micelles.<sup>23,26</sup>

The results presented here are focused on the cylindrical phase of the soft solid at 45°C. Rheology is used to measure the mechanical response as the system transitions from a liquid to a cylindrical phase. The magnitude of the complex modulus is measured as the temperature jumps from 5°C (liquid) to 45°C (cylindrical) using a fixed strain and frequency of 0.5% and 1rad/s.

SANS gathers structural information regarding the cylindrical phase. The 30m and 10m SANS instruments and rheometer used are the same as those describe in Section 4.2. The Couette cells used consist of a titanium cup (inner diameter = 29mm, 30mm, or 50mm) and a titanium bob (outer diameter = 27mm, 28mm, 48mm, or 49mm) to achieve 0.5mm to 1.5mm sample thicknesses. The samples are subjected to various thermal histories, cooled to  $5^{\circ}$ C for at least 30 minutes to eliminate structural history effects, and then heated to  $45^{\circ}$ C to form the cylindrical phase. After equilibrating at  $45^{\circ}$ C for 30-40 minutes, scattering is

collected for 5 minutes. The samples are sheared using a frequency of 5Hz and a strain ranging from 500% to 2500% for 4 to 8 minutes. Scattering is then collected 90 minutes after the cessation of shear.

The NG7 30m SANS instrument is used to gather scattering from 30wt% P103 with 3wt% BSA. A neutron wavelength of 6 Å and a  $\Delta\lambda\lambda$  of 0.115 is used to collect scattering at a sample-to-detector distance of 3.5m. The sample is loaded into a static cell that contains two quartz windows with a 2mm pathlength which mimics a parallel plate geometry. Temperature is controlled within ±1°C by a cell block that is heated and cooled by circulating ethylene glycol. The sample is loaded as a liquid and equilibrated at 5°C for 30 minutes to eliminate loading effects. This is followed by various thermal histories, cooling to 10°C (liquid), and then heating to 45°C to form the cylindrical phase. Scattering is collected for 5 minutes after 3 hours of equilibration. For all scattering data, standard reduction protocols developed at NIST are used to reduce the two-dimensional scattering patterns collected.<sup>27</sup>

# A.2 Results and Discussion

In Chapter 4, the impact of added BSA and lysozyme on the cylindrical phase of P123 and P103 soft solids is presented. As previously described, the samples are loaded in a Couette cell and heated from 5°C (liquid) to 45°C to form the birefringent cylindrical phase. The cylindrical phases have a HEX structure with the exception of the P123 composite with BSA which has a SQR structure and the P103 system with BSA has an assumed HEX packing.

Figure A.1 shows the thermal response of the P123 and P103 systems. The moduli values measured from the Rheo-SANS experiments are similar to the values measured in-house, leading to the assumption that the samples behave the same in the different experiments. Initially, the magnitude of the complex modulus is on the order of 10<sup>-1</sup>Pa. At approximately five minutes, the modulus rapidly increases by roughly five orders of magnitude.



Figure A.1: Time dependence of the magnitude of the complex modulus for the P123 and P103 neat and composite systems as the temperature jumps from 5°C (liquid) to 45°C (cylindrical). The samples are probed with small amplitude oscillations (0.5%, 1 rad/s). Results are for samples containing (a) 35wt% P123 and (b) 34wt% P103 or 35wt% P103 with 3wt% BSA or lysozyme in water. Moduli values measured during the Rheo-SANS experiments for the neat (•) and composite samples with 3wt% BSA ( $\circ$ ) and with 3wt% lysozyme ( $\Box$ ) are included. The samples used in the Rheo-SANS experiments have a solvent of 40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O.

After reaching the maximum, the behavior of the modulus is system dependent. The P123 neat and composite systems display varying behavior; the modulus of the P123 neat system gradually decreases over time whereas the P123 system with BSA displays a dip in the modulus. These differences are likely due to differences in unit cell structure. For the P103 neat and composite systems, the modulus decreases to a value that remains invariant with time, however, the magnitude of this value is dependent on formulation. The P103 neat and composite with lysozyme have approximately the same moduli values while the P103 composite with BSA has a modulus that is lower by two orders of magnitude.

Figure A.2 shows scattering collected at approximately 40 minutes after the temperature jump began. The solvent is protein matched (40.7mol%  $D_2O:59.3mol\% H_2O$ ) to isolate scattering from the polymer micelles. The formed cylindrical phase in the P123 and P103 composite systems display isotropic powder scattering typically produced by scattering from polycrystalline soft solids. The exception to this is scattering from the P103 system with BSA which has two distinct Bragg spots. A dashed line is drawn across the Bragg spots to help guide the eye. This anisotropic pattern demonstrates macroscopic alignment of the cylindrical micelles and suggests the added BSA is interacting with P103 micelles and inducing this alignment.



Figure A.2: Radial scattering patterns collected for the P123 and P103 neat and composite samples at  $45^{\circ}$ C at rest. Scattering is collected after the samples are equilibrated at  $45^{\circ}$ C for at least 40 minutes. The solvent is protein-matched (40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O).

To determine if this pre-alignment is an effect of the particular Couette cell used, Figure A.3 shows scattering patterns for the P103 system with BSA loaded in Couette cells of varying diameters and gap thicknesses. The scattering presented here is a small sample of our scattering library yet encompasses the general behavior of this composite system. Figure A.3 (a) is scattering for 30wt% P103 with 3wt% BSA in a static cell and is included to show that an isotropic powder pattern is gathered when the sample is placed between two parallel flat plates. When using a Couette geometry, scattering from the micelles always exhibits two equidistant Bragg spots. The dashed lines drawn across the Bragg spots are either tilted or parallel (Figure A.3 (e)) to the velocity vector. The angle that the dashed line deviates from the velocity vector is defined as the tilt angle ( $\phi_{tilk}$ ). The  $\phi_{tilt}$  describes the orientation of the cylindrical micelles relative to the

vorticity direction. A  $\phi_{tilt} = 0^{\circ}$  corresponds to Bragg spots along the equator and signifies the cylindrical micelles are aligned parallel to the vorticity direction (Figure A.3 (e)). A nonzero  $\phi_{tilt}$  indicates the micelles are tilted at an angle (~  $\phi_{tilt}$ ) with respect to the vorticity direction. The fact that the anisotropic scattering is only observed in the Couette cell and not in parallel plates suggests the alignment is a result of the curvature of the cell. In the Couette cell, this alignment is reproducible and insensitive to the degree of curvature and sample thickness. However, there is no trend between the tilt angle and the curvature or gap thickness of the Couette cell.





Figure A.3: Two-dimensional scattering patterns for P103 systems with added BSA at 45°C. The scattering is for (a) 30wt% P103 with 3wt% BSA loaded between two parallel plates, and (b)-(f) 35wt% P103 with 3wt% BSA in a Couette geometry. The cup diameter is (b)-(c) 29mm, (d) 30mm, and (e)-(f) 50mm while the bob diameter ranges between 27mm and 49mm to achieve a gap of 0.5mm or 1.5mm. The SLD of the solvent is matched to the protein (40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O) to isolate scattering from the polymer micelles.

To further highlight the symmetry and presence of the Bragg spots, Figure A.4 (a) shows the scattering intensity as a function of azimuthal angle ( $\phi$ ) for the primary ring in scattering patterns in Figures A.3 (b)-(f). The scattering curves are shifted horizontally by subtracting the  $\phi_{tilt}$  from the azimuthal angle. In Figure A.4 (a), all of the scattering profiles have peaks at 0° and 180°. This signifies that the Bragg spots have two-fold symmetry regardless of tilt angle.

A powder fraction  $(\phi_p)$  is estimated from the scattering to quantify the degree of alignment in the system. The powder fraction is the volume fraction of the system that is polycrystalline or oriented differently.<sup>28</sup> This value is calculated by dividing the minimum intensity ( $I_{min}(q^*,\phi)$ ) by the average intensity ( $I_{avg}(q^*,\phi)$ ) at a value of q\*, where q\* is the q position of the primary ring.<sup>28</sup> A  $\phi_p$  = 1 indicates the system is polycrystalline while a  $\phi_p = 0$  corresponds to a perfect single crystal.

$$\phi_{\rm p} = \frac{I_{\rm min}(q^*,\phi) - bkg}{I_{\rm avg}(q^*,\phi) - bkg} \tag{A.5}$$

Figure A.4 (b) shows  $\phi_p$  as a function of tilt angle for cylindrical phase of 35wt% P103 with 3wt% BSA in a Couette cell. The data in Figure A.4 (b) encompasses the scattering data in Figures A.3 (b)-(f) as well as other scattering data not presented. The tilt angle ranges from -25° to 15°, with a majority of the scattering have a tilt angle between -10° and 5°. The value of  $\phi_p$  ranges from ~0.4 to ~0.8 and has an average value of 0.67 that is denoted by the dashed line. Overall, the degree of alignment is approximately the same for all tilt angles.



Figure A.4: (a) Scattering intensity (I(q)) as a function of azimuthal angle ( $\phi$ ) for the primary ring of the scattering patterns in Figures A.3 (b)-(f). The data is shifted horizontally by subtracting the tilt angle ( $\phi_{tilt}$ ) from  $\phi$ . (b) Powder fraction as a function of tilt angle for 35wt% P103 with 3wt% BSA in a Couette geometry. The sample is loaded in Couette cells of varying dimensions (diameters, sample thickness), subjected to various thermal histories, and then heated from 5°C to 45°C to form the cylindrical phase. The dashed line denotes the average powder fraction.

To determine the impact of wall effects on the alignment, the beam is oriented parallel to the vorticity direction to probe the structure at multiple positions within the gap. The scattering data provides a projection of the crystal structure in the 1-2 plane. Figure A.5 (a) shows a schematic of the 1-2 Shear Cell used with the beam parallel to the vorticity direction. Figure A.5 (b) shows scattering collected near the inner wall, gap center, and outer wall. All of the scattering patterns display two Bragg spots, however, the tilt angle is dependent on gap position. Therefore, the alignment of the cylindrical micelles is not homogeneous throughout the gap. The tilt angles in these patterns (Figure A.5 (b)) suggest the cylindrical micelles are aligning with the cell wall and that the alignment is banded within the gap. The banded alignment is illustrated in Figure A.5 (c) which shows the alignment at the inner and outer walls to be opposite. This alignment agrees with the alignment displayed in the radial scattering (Figure A.3).



Figure A.5. Schematic of the 1-2 Shear Cell used (a). Scattering is collected near the inner wall, gap center, and outer wall. (b) Scattering from multiple positions in the gap for 35wt% P103 with 3wt% BSA in a protein-matched solvent (40.7mol% D<sub>2</sub>O:59.3mol% H<sub>2</sub>O). (c) Illustration of how the cylindrical micelles are oriented within the gap based on the scattering patterns in (b).

The P103 system with BSA is presheared using high amplitude oscillations with a fixed frequency of 5Hz and a strain between 500% and 2500% for 4 to 8 minutes. During shear, the scattering always displays two-meridional Bragg spots ( $\phi_{tilt} = 90^\circ$ ) similar to the neat system. Therefore, the cylindrical micelles align parallel to the velocity direction while subjected to shear.

However, this shear-induced alignment does not persistent after the cessation of shear. In Figure 4.8, the meridional Bragg spots divide and migrate toward the horizontal within the first 90 minutes following the cessation of preshear (500%, 5Hz for 8 minutes). The temporal evolution indicates the orientation of the micelles changes from the velocity to the vorticity direction.

The alignment of the micelles is approximately the same alignment prior to and 90 minutes after the cessation of preshear indicating a persistent alignment that is relatively insensitive to preshear.

Figure A.6 shows a selection of the scattering collected for the cylindrical phase after the cessation of varying degrees of preshear. The scattering is collected 90 minutes after the cessation of preshear or while the system is "at rest." Figures A.6 (a)-(c) show the scattering can have two equatorial spots, Figure A.6 (d) shows the Bragg spots can be tilted, and Figures A.6 (e) and (f) show the Bragg spots can be eliminated. The patterns correspond to the micelles oriented parallel to the vorticity direction, micelles oriented at an angle with respect to the vorticity direction, or a polycrystalline system, respectively. The overlying theme for all of the scattering is that the shear alignment does not persist.





Figure A.6: Two-dimensional scattering patterns for 35wt% P103 with 3wt% BSA collected 90 minutes after the cessation of shear. The samples are loaded in Couette cells of varying dimensions and subjected to different amounts of shear: (a) 29mm cup I.D., 1mm gap, 500% and 5Hz for 8 minutes, (b) 50mm cup I.D., 1mm gap, 1000% and 5Hz for 5 minutes, (c) 50mm cup I.D., 1mm gap, 500% and 5Hz for 5 minutes, (d) 29mm cup I.D., 1mm gap, 500% and 5Hz for 5 minutes, (e) 29mm cup I.D., 1mm gap, 2500% and 5Hz for 4 minutes, and (f) 29mm cup I.D., 0.5mm gap, 500% and 5Hz for 5 minutes.

In summary, there are three main conclusions from these results: 1) the added BSA induces long-range order of the P103 cylindrical micelles, 2) this alignment consistently occurs when using in a Couette cell, and 3) the BSA can persistently align the cylindrical micelles. The fact that the pre-alignment of the cylindrical micelles is formulation and geometry specific, leads to the postulation that the added BSA is interacting with the polymer. The interaction could be affecting the rigidity and persistence length of micelles which could be sensitive to the cell curvature. Furthermore, the demonstration that long-range order can be

initiated by the curvature the cell is important for the research communities utilizing Couette cells to study the flow and structure of wormy or rod-like micelle systems. While the alignment depends on the formulation of the system, it warns of the possible impact of cell curvature on the nature of rod-like micelles.

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