Small Angle Neutron Scattering of Rotating Nanostructured Thin Films

Table of Contents

Synopsis and Objective of Experiment:

In this study, we will utilize Small Angle Neutron Scattering (SANS) to measure the nanometer scale assembly of a diblock copolymer after spin casting on a silicon substrate. The block copolymer will self-organize into a morphology that features cylinders 10-80 nm in width and lengths on the order of microns or larger. This morphology can be characterized by the orientation distribution of the cylinders relative to the plane of the substrate. The important concepts developed in this module are as follows:

- Small Angle Neutron Scattering measures the time averaged structure of matter by measuring the elastic scattering function (essentially a fourier transform of the positions of all of the molecules).
- This technique is particularly useful in the length scales of nm's to 100's of nm.
- By measuring our sample at many angles of incidence, accomplished by rotating the sample in the beam, we are able to determine the orientation distribution of the cylinders relative to the substrate.

1. Assembly of Diblock Copolymer Films

Block copolymers are an important class of soft materials, useful because they literally combine two different molecules into one, providing the capability to utilize the properties of both of the individual molecules at one time. A polymer molecule, usually represented as a string-like chain of individual components (or "mers"), can be attached at its end points to another chain. Since the blocks tend to be constructed of immiscible species, the two blocks would prefer to separate into two macroscopic regions. This macrophase separation causes oil to separate from water into two macroscopic layers in a beaker. However, in a block copolymer, the blocks are covalently linked and cannot be forced apart over distances larger than the molecular size. The result is a “microphase” separation, where molecules organize in such a way as to minimize the surface area between the block-rich phases, while simultaneously minimizing the entropic penalty of stretching the chains. As a result, microphase separated diblock copolymers feature a wide range of potential morphologies where the domains are typically 10-100 nm in size. Morphologies can include spheres, cylinders, lamellae, and a variety of interconnected sponge-like morphologies.

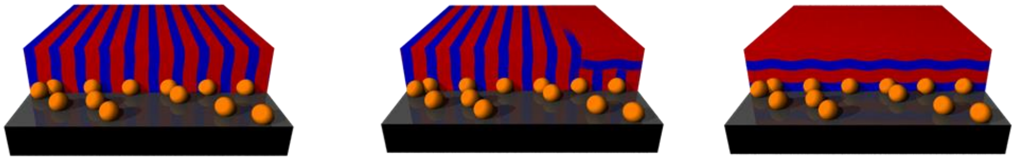

Figure 1. A schematic of three potential orientations of a lamellar forming diblock copolymer on a substrate where interactions are controlled with nanoparticles. The orientations shown are perpendicular to the substrate (left), a mixture of parallel and perpendicular (middle), and parallel to the substrate (right). The final two cases show schematically how a distribution in orientation may be revealed by SANS. For the case in the middle, there are two distinct populations that will be observed, however in the case on the right, the orientation will be seen as a distribution centered on the parallel orientation.

While the interaction between the two phases often determines the equilibrium morphology, the orientation of that morphology can be controlled through both equilibrium and dynamic processes incurred during film formation. Given that there are two blocks with very different enthalpic interactions, a substrate that is more enthalpically favorable to one of the blocks will naturally adsorb that block preferentially. For lamellae, this can drive a series of lamellae alternating on the substrate as seen in figure 1. For surfaces that are equivalently attractive to both blocks, often known as “neutral” surfaces, the block copolymer could choose to orient perpendicular to the substrate. Additional orientations are possible given a variety of process conditions, providing a potential route to a wide range of options in creating nanostructured materials.

2. Small Angle Neutron Scattering

Neutron scattering measures the change in momentum (mass and velocity) of the neutrons as they pass through the material and interact with nuclei. This change in momentum can reveal information about the structure (usually in elastic scattering) and motions within the material (typically seen in inelastic scattering). In contrast to x-ray scattering or visible light scattering, neutrons interact with the nuclei and not the electron cloud. As a result, neutrons often have very different interactions with a given material than those seen with electromagnetic radiation. This makes neutron scattering very complimentary to techniques that rely on electromagnetic scattering.

All neutron techniques interact with nuclei, however different techniques measure different properties of the neutron as they pass through the material. Small Angle Neutron Scattering (SANS) measures the elastic scattering function of the neutrons, meaning there is an inherent assumption that the neutrons have not lost energy (or changed wavelength) as they passed through the material. In most cases, this is a sufficient assumption. As in other forms of neutron scattering, SANS measures the change in momentum of the neutrons, where the momentum is defined as ½ m * **v**, m is the neutron mass and **v** is a vector of the neutron velocity (vectors are denoted here as boldface letters), In the assumption of elastic collisions, the magnitude of the m and **v** are constant. As a result, we are able to measure the momentum change, **Q**, by simply measuring the change in direction of the neutron upon scattering:

$$|\mathbf{Q}| = |\mathbf{k}_o - \mathbf{k}_i| = 4\pi/\lambda \sin(\theta) \qquad \text{(Eqn. 1)}$$

Here, the change in momentum is simply the difference in outgoing ($\mathbf{k}_o$) and incident ($\mathbf{k}_i$) momentums, and can be expressed using simple vector mathematics as an inverse function of wavelength (λ) and a trigonometric function of the half angle of scatter between the outgoing and incoming neutrons (θ). At small angles, note that $\sin(\theta) \sim \theta$. This relationship is often useful in back of the envelope estimates, however we will be using the full expression for our measurements. Since the wavelength is assumed constant, the SANS experiment is simply the measurement of scattered neutron intensity as a function of scattering angle at fixed wavelength, providing us with I(**Q**).

3. Differential Cross Section and Characteristic Length Scales

The probability that a nucleus will scatter neutrons at a particular angle is given by the equation for the differential cross section:

$$\frac{d\Sigma(Q)}{d\Omega} = \left(\frac{N}{V}\right)\Delta\rho^2 V_P{}^2 P(Q) S_I(Q) \qquad \text{(Eqn. 2)}$$

Where N/V is the density of particles, V_P is the particle volume, and ρ is the scattering length density. P(Q) and S(Q) are the form factor and structure factors, representing the Q dependent scattering from the individual particles and the interactions between the particles respectively. The form and structure factors for a variety of systems have been derived and can be found in the literature. The form factor is often simply the Fourier transform of a function defining the real space shape of the particle. As an example, the form factor for a sphere of radius R is given as the following equation:

$$P(Q) = \frac{2}{Q^4 R_g{}^4}\left[\exp(-Q^2 R_g{}^2) - 1 + Q^2 R_g{}^2\right] \qquad \text{(Eqn. 3)}$$

The scattering length density, ρ, is the natural probability of a given species (the "species could be a nucleus, or a particle, or a phase, etc) to scatter neutrons. This is analogous to the index of refraction in visible light. In order for two phases to scatter coherently, there must be a significant difference in their values of ρ, meaning Δρ must be significant. The value Δρ represents the inherent contrast within the system. If you have a multicomponent system, and would like to make a component invisible (so that you can measure the other components more precisely), it is possible to use isotopes to change the value of dr in your system. This is called contrast matching, and it is one of the most powerful components of neutron scattering in soft materials. In the case of the block copolymer film, the contrast is achieved by using a deuterated block, where the hydrogens normally attached to the chain have all been replaced with their isotope. By only deuterating one of the blocks, the contrast between the blocks, Δρ, then allows us to evaluate equation 2.

Given sufficient contrast, the characteristic length scale of the morphology, d*, is expected to occur throughout the material. In the case of microphase separation, this fourier transform of the expected morphology will feature a peak at a corresponding value of q, where q*=2π/d*. While a full model of the morphology is possible, involving both the structure and form factors, we will employ a simple empirical model to extract this length scale and the associated intensity at q*. The empirical fit will follow the following equation:

$$I(q) = \frac{C}{(|q - q^*|x)^m} \qquad \text{(Eqn. 4)}$$

where C, m, and x are empirical constants. This function provides a peak at a characteristic q-vector, q*, and can be fit to provide the intensity I*(q). For each angle, this information is collected and fit, and then plotted as a function of the sample rotation angle, ω. Samples that have isotropic orientation distributions will have an unchanging I*(ω) and q*(ω). Samples that have preferred orientations will have variations in both quantities. As an example, a sample with lamellae perfectly oriented perpendicular to the substrate would have a peak I*(ω) when the substrate normal was oriented parallel to the beam direction. This corresponds to the condition of the direction of q pointing in the direction of the lamellae normal vector.

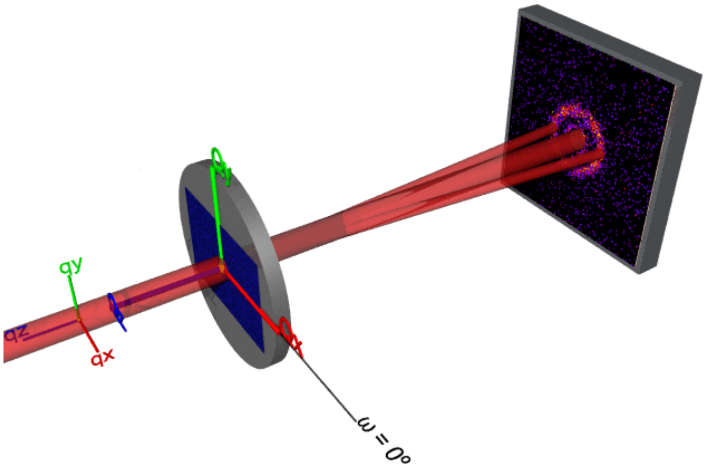

Figure 2. Schematic of the SANS experiment with a rotating sample. The angle of rotation, ω, is indicated in the schematic. The convention used for this experiment is ω = 0 deg when the surface normal of the substrate is parallel to the incident beam direction. Also shown is the direction of q_x and q_y, where q_x is perpendicular to the rotation axis.

4. Sample Preparation

Samples are prepared by spin coating deuterated poly(styrene)-block-poly(methyl methacrylate) from solution in toluene onto a silicon substrate. After deposition, the samples are annealed in an oven for varying amounts of time. The annealing time in this case is used to create variations in the amount of ordering achieved in the sample, with longer annealing times providing more orientation. A native oxide layer that grows on the silicon substrate prefers the poly(methyl methacrylate) block, driving the creation of lamellae oriented parallel to the substrate at the surface. A similar effect at the vacuum surface tends to drive the poly(styrene) layer to adsorb there. However, chemical modifications of the substrates have been used to vary the attraction of the blocks to the silicon substrate, providing an opportunity to drive the average orientation of the block copolymer films using the annealing time.

5. Configuring the 10m SANS Instrument

The 10m SANS utilized for this module is named to reflect the largest possible distance between the first beam defining aperture and the detector. In fact, for a given experiment, the first thing we must accomplish is to determine the necessary optical configuration to achieve the range of Q required for the experiment. Often, an experiment requires measurements at multiple configurations to span a larger range of Q. As shown in figure 2, the neutrons for the 10m SANS pass through a velocity selector first. This selector is used to choose the average velocity, or wavelength, of the neutrons passing through the sample. After passing through some other optics in the pre-sample flight path, the neutrons pass through the sample located in a sample chamber. They are then scattered into a large vessel that contains the neutron detector, and the intensity and angle of the scattered neutron wave is measured and recorded.

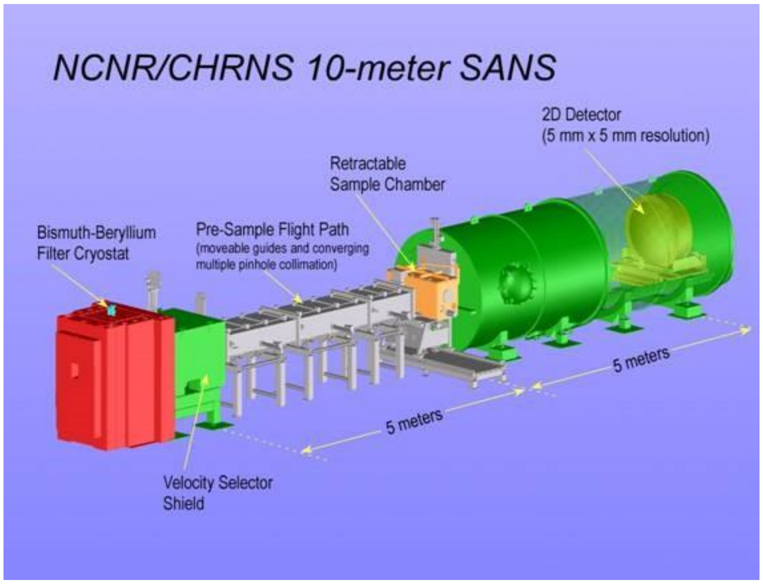

Figure 3. Schematic of the 10 meter Small Angle Neutron Scattering (SANS) instrument at the NCNR. The 10 meter designation refers to the longest possible pre-sample optical path for the neutrons of 5 meters, and the longest possible post-sample detector distance of 5 meters, for a total instrument “length” of 10 meters. Also shown are the locations of the velocity selector, which is used to determine the wavelength of the neutron beam, and retractable sample chamber where the rotation stage is mounted, and the filter cryostat used to remove unwanted radiative contributions to the beam.

The 2-dimensional neutron detector is placed after the sample at a specified distance and lateral position. In our case, the pixels are arranged in a square array, where the pixel-to-pixel distance is constant. The pixels are 0.5 cm X 0.5 cm in size. By choosing different detector distances, we can change the range of angles measured by the instrument. At long detector distances, we will observe smaller values of q ($q \rightarrow 0$ in equation 1). Conversely, if we move the detector closer to the sample, we will observe larger angles and larger values of q. Note that the fixed pixel size determines the minimum angle resolvable at any given detector distance.

6. Collecting Data

Thin films will be mounted in a rotation stage within the sample chamber. To collect the maximum range of q vectors possible at a given rotation angle, we will employ three configurations capturing a high, intermediate, and low values of q. The configurations will be based on a beam of 0.25 inches in diameter as defined by the sample aperture. As illustrated in equation 1, we will utilize three configurations where the detector distance and wavelength are varied to achieve the different q ranges. We will rotate the sample between data collection times in order to vary the direction of the q vector relative to the sample substrate. By mapping I(q, ω), we are able to establish the structure over a 3-dimensional space within the film. For this experiment, we refer to the rotation angle as ω = 0 degrees when the beam direction is parallel to the surface normal (q is parallel to the substrate). The experiment will collect 2 dimensional scattering images for sample orientations of approximately -70 degrees to +70 degrees, in single degree increments.

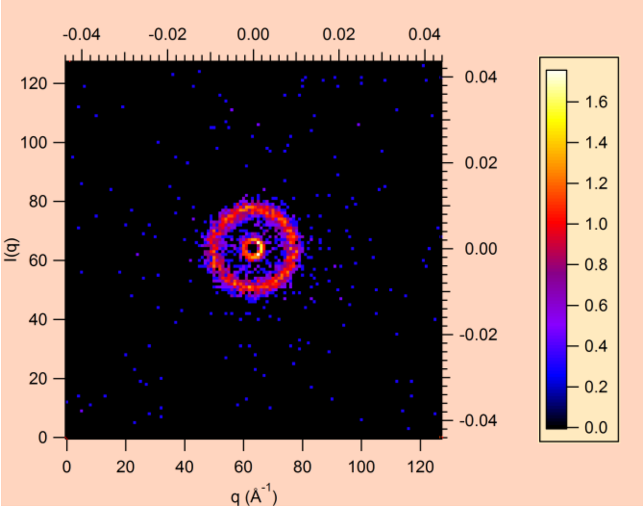

Figure 4. Logarithmic intensity, prior to background subtraction, plotted as a 2-dimensional detector image. The value of the logarithmic intensity is given by the scale color bar on the right. The data is collected from a block copolymer film measured with the beam perpendicular to the substrate (ω=0 deg). The characteristic length scale of the lamellar morphology is indicated by the peak in intensity. The uniform ring indicates that the morphology is isotropic in the plane of the substrate. In this scenario, q_x is horizontal and q_y is vertical on the image.

7. Data Reduction

During data collection, we will measure a sample over a range of incidence angles. In addition, for each incidence angle, we will measure the sample at three instrument configurations (high, intermediate, and low q). These files will then be collected and the data reduced using the standard NCNR algorithm for data reduction. In this algorithm, each 2-dimensional scattering image processed by subtracting the q-dependent background of the empty cell (i.e. a substrate without a sample) and the q-dependent background of the instrument. The empty cell in this case is a substrate without a sample, and the q-dependent background of the instrument is measured by blocking the beam during data collection. These terms are weighted using a ratio of the sample transmission to the empty cell transmission. The entire data reduction algorithm is summarized through the following equation:

$$I_{Absolute} = A\left\{\left[I(q)_{Sample} - I(q)_{Blocked\ Beam}\right] - \frac{T_{Sample}}{T_{Empty\ Cell}}\left[I(q)_{Empty\ Cell} - I(q)_{Blocked\ Beam}\right]\right\}$$

(Eqn. 5)

where $I_{Absolute}$ is equivalent to the differential cross section, A is a scaling constant that includes the sample volume, beam flux, and other q independent factors, and T represents the transmission of the sample relative to the open beam flux. After the 2-dimensional data is placed on an absolute intensity scale, where the units are cm^{-1}, the absolute intensity can be integrated to obtain the 1-dimensional function I(q).

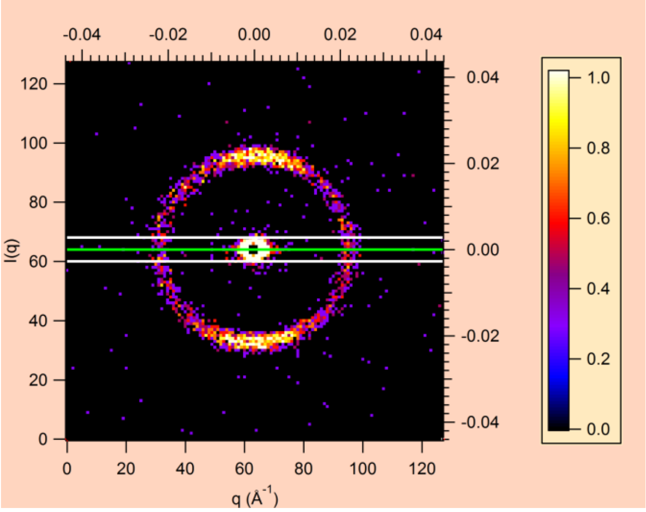

Figure 5. Data from an oriented block copolymer film when the sample is rotated to ω = +50 deg. The orientation of the sample means a circular average is inappropriate, and a rectangular, or box, average must be used to integrate the data into a 1-dimensional form as illustrated here with the white box. The green line indicates the value of q_y used occurs in the center of the width of the box.

In contrast to isotropic samples such as polymer solutions, the scattering in this experiment cannot be integrated with a circular average. For oriented samples, we expect I(q) to be different along differing directions within the sample. In this case, we desire to process only the scattering along the q vector perpendicular to the sample rotation axis, which we label q_x as seen in figure 1. For each value of ω, we will use a box average to obtain the function $I(q_x, \omega)$.

8. Data Analysis

Once we have the data in absolute intensity form, the data is fit using a freeware open source program, SASView (www.sasview.org). The 1-dimensional data sets all feature a single, broad based peak at an intermediate q value. The objective of our data analysis is to extract the function I(q*, ω). To achieve this goal, the individual data sets are loaded into SASView and fit using the "broad peak" model. The broad peak model follows equation 4, with fit parameters of C, m, q*, and ξ. The value of C is used to obtain the peak intensity, I(q*), where q*occurs at the center of the peak. The data can then be plotted as I*(w), where I* = I(q*). A sample data set is plotted in figure 6 for two films. In this example, one of the films is isotropic, while the other shows significant orientation.

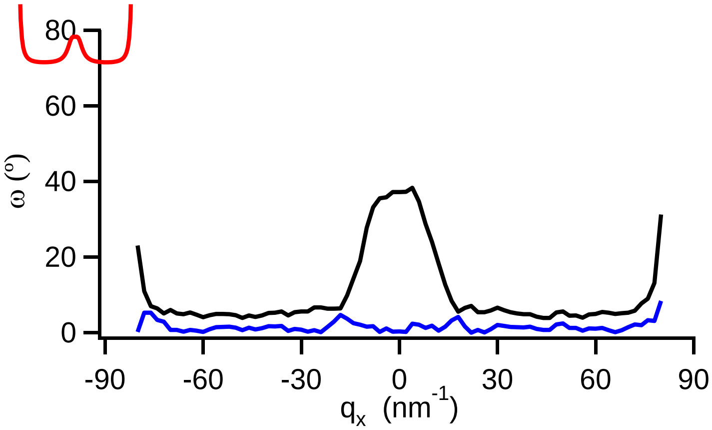

Figure 6. The final plot of I(w) for two films with different orientation distributions.

The isotropic film, shown in the blue data set, has a uniform intensity as a function of sample rotation angle, indicating that the morphology is isotropic in the plane perpendicular to the substrate. By examining the data at w=0 such as in figure 4, we can further state that the morphology is isotropic in all 3-dimensions. In contrast, the peak of the data in the black data set, further fit with a simple orientation distribution function shown in red, shows two preferred orientations at w=0 deg and w=+/- 90 deg (parallel and perpendicular to the substrate respectively). Furthermore, since the intensity is proportional to the number of structures within the film, it is correct to state that the fraction of lamellae oriented parallel to the substrate is far greater than those oriented perpendicular to the substrate. Since we cannot access ω = 90 deg directly with SANS, we would require a further measurement with neutron reflectivity (which provides information ONLY at ω=90 deg) to provide a quantitative ratio of the two distributions.