

# Measuring Complex Fluids with RheoVSANS

## Introduction to RheoSANS

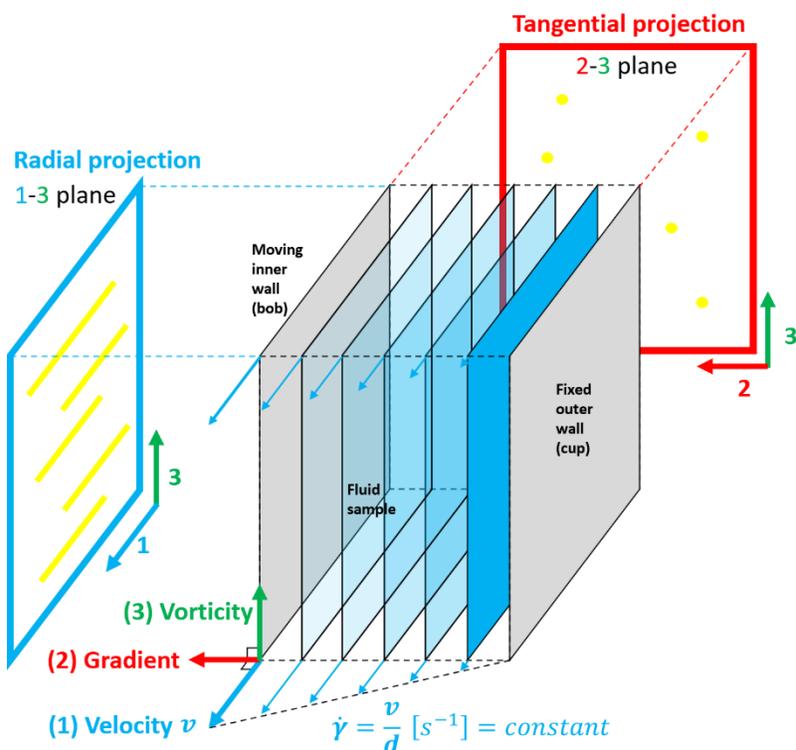
Complex fluids are a broad class of materials that exhibit unique mechanical responses and often consist of multiple components. Blood, foams, paints, polymer suspensions, emulsions and granular materials are a few examples of complex fluids. Because the form and properties of these fluids vary greatly, they are used in a variety of applications including lubricants, paints and coatings, food processing and many household products. The diverse nature of these materials can make them challenging to characterize and process. Nearly all complex fluids undergo flow during processing into a final product, and each fluid responds differently to the flows experienced in processing equipment. To optimize material performance, it is necessary to understand how these fluids will respond to different flow fields prior to scale-up and large-scale production. The field of rheology, or the study of flow, strives to better measure the flow properties of complex fluids and aims to understand how changes in their underlying microstructure affect the macroscopic mechanical properties.

A rheological instrument, otherwise known as a rheometer, subjects fluids to different flow fields and measures the mechanical response of the fluid under different flow conditions and sample geometries. From these measurements, a material's response during processing can be predicted, and equipment is designed to accommodate this mechanical response. When subjecting a material to particular steady shear rate,  $\dot{\gamma}$ , the fluid response is recorded using the shear stress,  $\tau$ , or force per unit area, required to deform the fluid at this rate. Because complex fluids often contain multiple components, it is common for the fluid micro- and nanostructure to deform or rearrange during flow. These structural changes are often the physical source of the observed rheological properties, including the shear stress response, viscosity and normal stress differences. Complex fluid architecture is thus critical to product performance, and rheology helps direct design of material architecture.

While viscometry and rheometry techniques *indirectly* probe changes in the fluid structure, scattering techniques such as small-angle neutron scattering (SANS) can provide *direct* measurement of fluid structure while it is flowing. During a RheoSANS measurement, a beam of neutrons is directed at a fluid sample positioned within a rheometer. While most of the neutrons “transmit” or pass right through the sample, some neutrons can “elastically scatter” or change momentum through a change in scattering angle at fixed neutron energy or wavelength  $\lambda$ . The corresponding neutron intensity ( $I$ ) measured as a function of scattering angle or scattering wavevector magnitude, given by  $q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$ , is related to particular fluid structures that contain different scattering length densities. The pattern generated by this scattering can be analyzed to determine particle shape, size, polydispersity, and particle orientation relative to an imposed flow field. By combining SANS with rheological measurements, it is possible to observe shear-dependent structural changes in the scattering pattern, while simultaneously measuring rheological properties. This unique pairing of characterization techniques, known as RheoSANS, provides a powerful tool for material scientists to study complex fluids from a macroscopic and microscopic perspective.

The NIST Center for Neutron Research provides a suite of RheoSANS instruments capable of measuring the nanostructure of complex fluids in motion, including a 1-3 and 2-3 RheoSANS instrument, a 1-2 shear

cell, Dielectric RheoSANS, MicroRheoSANS, Capillary RheoSANS, and Extensional rheoSANS. This experiment will focus on the more traditional RheoSANS setup consisting of a rotating concentric-cylinder geometry (Couette cell or cup-and-bob) which is positioned on the very-small-angle neutron scattering (VSANS) beamline. The experimental setup is capable of measuring scattering from the flow velocity-vorticity (1-3) and velocity gradient-vorticity (2-3) planes separately (Figure 1). As will be discovered in this experiment, measuring both the radial (1-3) and the tangential (2-3) projections of the sample under flow helps to better quantify the fluid structure and particle orientations that exist in all three dimensions.



**Figure 1:** This experiment assumes laminar (sheet-like) flow of the sample in a small gap ( $d = 0.5$  mm) positioned between rotating concentric cylinders, in which the shear rate (or velocity gradient) is constant throughout the gap. This simple shearing flow type is produced by an moving inner wall (bob geometry) and a fixed outer wall (cup geometry). The flow velocity, gradient, and vorticity vectors are orthogonal (at right-angles to one another) and are designated by blue, red, and green arrows, respectively. The two scattering plane projections in this experiment are the radial projection (velocity-vorticity or 1-3 plane) and the tangential projection (gradient-vorticity or 2-3 plane).

### Primary Experimental Goals and Learning Objectives

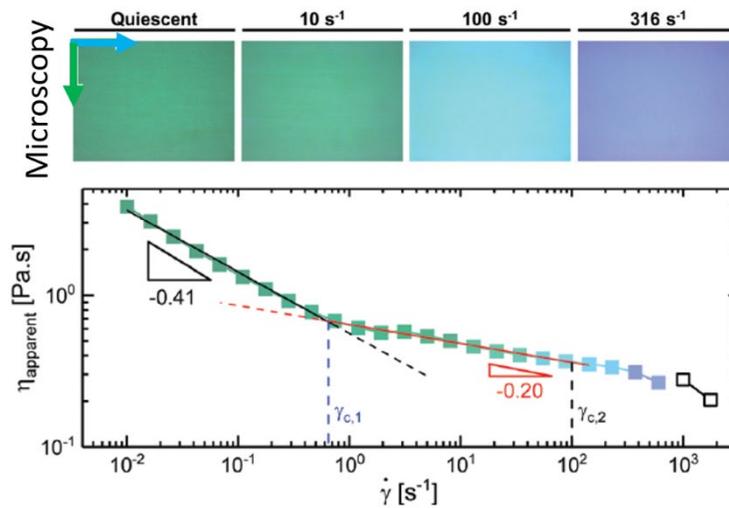
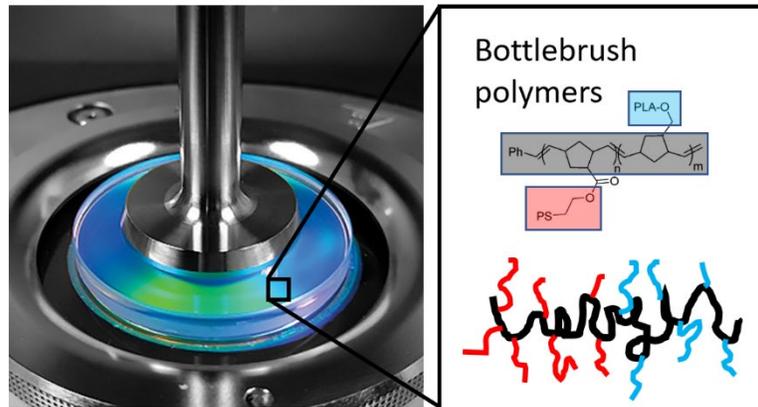
1. Characterize a bottlebrush copolymer solution using RheoVSANS to determine what causes these solutions to change color with increasing shear rate during steady shear flow.
2. Reduce 2D VSANS data for 1-2 and 1-3 shear planes and connect features in scattering data to material structure and behavior

3. Apply several 2D analysis techniques on scattering data to grow understanding of RheoSANS characterization capabilities and explore the relationship between shear rate, fluid alignment, mechanical properties and optical properties

### **Bottlebrush polymer solutions**

Bottlebrush polymers are a class of high molecular weight polymers consisting of a single linear backbone with a series of side chains densely grafted along the length of a linear backbone (Figure 2). The bottlebrush side chains sterically repel their neighbors and cause the linear backbone to elongate and result in less polymer entanglement. Both the side chain length and side chain spacing influence these steric forces. Synthesis of bottle brush polymers is typically done by grafting side chains onto the polymer backbone. The mechanical, optical and chemical properties of these polymers can be easily tuned by grafting side chains with desirable attributes and adjusting the length and spacing of the side chains.

In this module, the material under examination is a poly(styrene)-*b*-poly(lactic acid) (PS-*b*-PLA) di-block bottlebrush polymer (Figure 2). PS and PLA were chosen as branches because of the difference in their optical properties and specifically their refractive indices. By having blocks with different refractive indices, it is possible to produce a material that can selectively reflect specific wavelengths of light and thus produce color. For a simplified case, the wavelength of reflected light for a two-layered material can be calculated by  $\lambda_{calc} = 2(n_1d_1 + n_2d_2)$ , where  $n$  is the refractive index and  $d$  is the layer spacing for the two different layers. In this way, the PS-*b*-PLA polymer studied here produces the green color seen in Figure 2 under quiescent conditions (at rest). An example of an optical rheological measurement is also shown in Figure 2. When subjected to flow, this bottlebrush polymer solution shear thins and undergoes a color transition to cyan/indigo with increasing shear rates, and eventually loses all observable color at the highest shear rate. Identifying the underlying cause for this shear-dependent color transformation using RheoVSANS is the primary objective of this module.



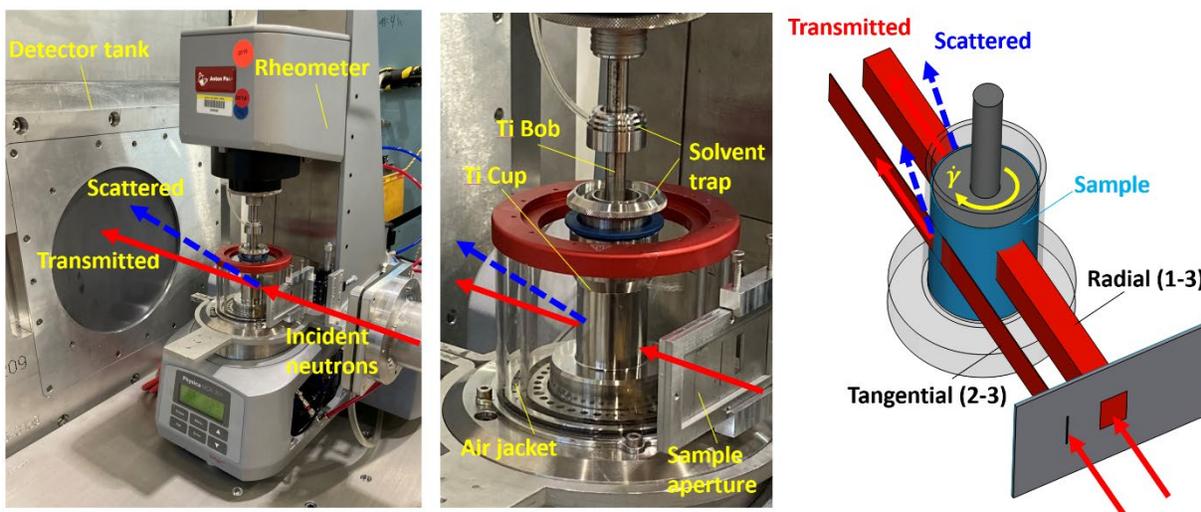
**Figure 2:** The sample of interest consists of a diblock bottlebrush polymer poly(styrene)-*b*-poly(lactic acid) (PS-*b*-PLA) in deuterated toluene. Light microscopy shows a change in color from green to blue to violet as the shear rate increases, eventually losing observable color at a shear rate of 1000 s<sup>-1</sup>. Below is the sample viscosity as a function of the shear rate. Since neutron beamtime is a limited resource, and not all shear rates can be measured, what particular shear rates would you suggest to measure with RheoVSANS?

### RheoVSANS Measurements

A rheometer fitted with a Couette cylinder geometry (titanium bob with quartz cup) is placed on the VSANS beamline (Figure 3). The sample, PS-*b*-PLA in deuterated toluene, is placed between the concentric cylinders and is subjected to shear rates between 0.01 s<sup>-1</sup> and 1770 s<sup>-1</sup>. To fully characterize the material structure, it is necessary to conduct scattering through both the flow-vorticity (1-3) and flow gradient-

vorticity (1-3) shear planes (Figure 1). Both of these measurements are done using the same rheometer setup. To view the 1-3 shear plane, the neutron beam is aligned through the middle of the cylinders along the radial direction (Figure 3). The 2-3 shear plane is viewed by aligning the beam along the tangent of the annular gap between the cylinders. The tangential setup requires a much thinner sample aperture than is used in the radial setup. This thin aperture narrows the beam so that neutrons only pass through the annular gap.

VSANS has the unique ability to measure scattering over a broad  $q$  range simultaneously by using multiple detectors. To measure the scattering patterns produced by the PS-*b*-PLA bottlebrush polymers, the four front detectors are arranged 4.2 m from the sample, and the two middle detectors are placed 19.4 m from the sample. Together these detectors are capable of *simultaneously* capturing scattering over a  $q$  range of  $0.0027 \text{ \AA}^{-1}$  to  $0.048 \text{ \AA}^{-1}$  when using a single guide (NG1) and  $5 \text{ \AA}$  neutrons.



**Figure 3:** The rheometer configured with rotating concentric cylinder geometry (cup-and-bob) at the VSANS beamline. A closer view of the experimental setup shows the rotating titanium bob, titanium cup, surrounding air jacket for temperature control, solvent trap for mitigating evaporation, and sample aperture for radial scattering (1-3 plane) and tangential scattering (2-3 plane). The rheometer hardware and software controls the velocity of the rotating inner bob, which defines the shear rate  $\dot{\gamma}$ , and also measures the shear stress  $\tau$  to determine the shear-dependent sample viscosity  $\eta(\dot{\gamma}) = \frac{\tau}{\dot{\gamma}}$  at each shear rate.

Together, we will work through and discuss the following experimental steps necessary to address our objectives:

### Experiment check list:

- Experiment setup
  - Rheometer setup (Fig. 3)
  - VSANS configurations (radial and tangential)
- Scattering measurements
  - Measure the *Open beam transmission, Blocked beam scattering, Empty cell transmission & Empty cell scattering, Sample transmission & Sample scattering*
  - Repeat sample transmission and scattering measurements for both the radial (1-3) and tangential (2-3) beam configurations.
  - Repeat the scattering measurement at each desired shear rate
- File reduction
  - Start Igor and load VSANS macros
  - Calculate transmissions for the *Empty cell* and all *Sample scattering* files for both the radial and tangential configurations.
  - Build a reduction protocol to reduce the full 2D data (QxQy)
  - (Optional) Build a reduction protocol in Igor to perform sector and annular averages at defined sector angles and sector widths ( $\phi \pm \Delta\phi$ ) and defined annulus center and annulus width ( $q \pm \Delta q$ )
  - Reduce multiple files using the saved reduction protocols
- Plotting data
  - Load the reduced files (.ABS file type) into SasView software for additional plotting, fitting, and analysis
  - Sector and annular averages can be constructed by right-clicking on the 2D data file in SasView. Perform sector and annular averages at defined sector angles and sector widths ( $\phi \pm \Delta\phi$ ) and at defined annulus center and annulus width ( $q \pm \Delta q$ ).
- Analyzing and discussing data
  - Identifying structures at low q (larger length scales) and high q (smaller length scales)
  - Analyze and discuss any q-dependent changes in sector-averaged peak positions or peak widths, both in 1-3 (radial) and 2-3 (tangential) planes. How are these features oriented with the flow velocity direction? How do these features change with shear rate? What might the peak positions or peak widths physically relate to in the sample?
  - Discuss any  $\phi$ -dependent (azimuthal angle or orientation angle) changes, both in the 1-3 and 2-3 planes at different shear rates. What do orientation changes physically relate to in the sample?
- Conclusions
  - Provide your best description for how the nanostructure of bottlebrush polymer solutions change when at rest and when under steady shear flow. Why might the sample color change with shear rate? Why does the sample color disappear at the highest shear rates? Why might the sample viscosity depend on the shear rate?
  - What could be designed and engineered at the molecular level for future iterations of bottlebrush polymer materials, in order to achieve a different rheological response and/or a different change in color?

## **Practical considerations for RheoSANS experiments:**

Below is a practical guide on things to think about and to estimate/calculate/measure prior to any RheoSANS measurement. Thinking about how each point relates to your sample will help you take advantage of the neutron scattering technique and maximize your hard-earned beamtime.

### **Characteristic length scales of your sample**

An estimate of the characteristic length scale of your sample could be a primary particle diameter, radius of gyration, aggregate or cluster size, mesh size, pore size, etc. Unless the sample is opaque to visible light (even when diluted at lower concentrations), these length scales are more easily and quickly obtained using visible light scattering. Regardless, the q-range you want to measure should adequately span  $q \approx \frac{2\pi}{D}$ , where D is the characteristic length scale of interest

### **Characteristic time scales of your sample under flow**

Assuming that you have already measured a steady-shear flow curve (viscosity as a function of shear rate) or frequency sweep (linear or non-linear viscoelastic regime), the onset shear rates for shear thinning, shear thickening, or crossover frequencies are typically regions of interest for microstructural measurements. Consider always measuring your sample “at rest” for a basis of comparison of the microstructure when “under flow”, as this also allows for subtraction of the two scattering measurements to identify the change due to the imposed flow field. Also consider collecting at least one or two shear rates or frequencies above and below this characteristic change to obtain a better understanding of the extent of the microstructural change.

### **Chemical composition of the sample and solvent**

Without contrast between the scattering length density (SLD) of your solvent and your sample of interest, there will be no coherent neutron scattering! Thus, elemental composition and concentration is necessary to estimate the scattering contrast between your sample and the surrounding solvent. Use the online scattering length density (SLD) calculator: <https://www.ncnr.nist.gov/resources/activation/>. Typically, it is easier to implement commercially available deuterated solvents rather than deuterating the sample itself. Composition is also necessary to determine the sample activation and half life, which can also be estimated using the same website. The website will also estimate the sample transmission if given a particular composition, neutron wavelength, and sample pathlength. This will help determine which gap size (currently 0.5 mm or 1 mm) is best to maximize count rate while avoiding multiple scattering effects.

### **Rheology**

Often, but not always, if there are significant changes in the macroscopic rheological response, then there are significant changes in the underlying microstructure that might be measurable. Of course, for SANS measurements, the microstructure must be changing at the appropriate length scale, with SLD contrast, and within the accessible q-range (see above). Likewise, if the rheology is not changing significantly with shear rate or applied frequency, then the microstructure is likely not changing significantly and the RheoSANS method is unnecessary. If this is the case, then sample is probably better

suited for simple “static” SANS measurements in the typical demountable cells. A static SANS experiment can step through many different sample compositions as compared to RheoSANS, because it simply takes longer (1-2 hr) to swap samples during a RheoSANS experiment.

### **Sample stability concerns**

Concern for the stability of your sample could be a sedimentation time or phase separation time after which the sample is no longer the same concentration or composition *in the path of the neutron beam*. Since RheoSANS measurements typically take 30 min to 4 hours at each shear rate, you will want your sample consistent over the measurement time period. Solvent evaporation can be mostly mitigated by the use of a solvent trap. However, if near a critical concentration or temperature, small amounts of inevitable solvent evaporation may be important to monitor and adjust conditions.

### **Scattering count times**

It is always a good idea to ask yourself: how long should I count? The signal-to-noise ratio decreases as the square-root of count time, meaning if you count for 4 hours instead of 1 hour, your signal-to-noise ratio increases by a factor of 2, or if you count for 16 hours instead of 1 hour, your signal-to-noise increases by a factor of 4. With that in mind, typically sufficient scattering counts for a 1D curve (Intensity vs.  $Q$ ) requires  $10^5$  counts on any detector. However, RheoSANS measurements and analysis typically average smaller sections of the 2D detector, such as when analyzing a sector average or an annular average. Note that the two dimensions are  $Q_x$  and  $Q_y$ , where  $Q = (Q_x^2 + Q_y^2)^{1/2}$ . This is why RheoSANS measurements typically require approximately 1 order of magnitude more counts to allow for reasonable signal-to-noise when taking an annular average or sector average of the 2D data. Thus, a rule of thumb is to aim for  $10^6$  counts at each shear rate for RheoSANS measurements, but it could be more or less depending on your analysis count-averaging method.

Once the sample is loaded into the rheometer, perform a count rate check for 60 s to determine the count rate at the detector with the lowest neutron flux, which will be the detector farthest back from the sample or at the lowest  $q$ -range. Use this measured count rate to calculate the time needed to reach approximately  $10^6$  counts on the detector, using  $\text{Count Time [s]} = 10^6 \text{ [counts]} / \text{Count Rate [counts/s]}$ . If this count time is relatively small, on the order 1 hour or less, then consider if you want to count for 4 times as long to improve signal-to-noise by a factor of 2. Depending on your analysis averaging method and the scientific question you are trying to answer, choose whether to count for 1 hour at 4 different shear rates (4x shear rates but with 1x signal-to-noise), or whether to count for 4 hours at one shear rate (0.25x shear rates but with 2x signal-to-noise).